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Application No. 10/771,674

DECLARATION

I, Machiko Shoji, a staff member of TAIYO, NAKAJIMA & KATO, 3-17, Shinjuku 4-chome, Shinjuku-ku, Tokyo 160-0022, Japan, do hereby declare that I am well acquainted with the English and Japanese languages and I hereby certify that, to the best of my knowledge and belief, the following is a true and correct translation made by me into the English language of the accompanying copies of the documents in respect of Japanese Patent Application No.2003-29780 filed on 6th February 2003 in the name of FUJI PHOTO FILM CO., LTD.

Dated this 11th day of September 2006

Machiko Shoji

Machiko Shoji

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[TITLE OF THE INVENTION]

PHOTOTHERMOGRAPHIC MATERIAL

[CLAIMS]

[Claims]

[Claim 1] A photothermographic material comprising, on a support, a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder, wherein the photothermographic material comprises a compound having a group adsorptive to silver halide and a reducible group or a precursor of the compound, a silver behenate content of the non-photosensitive organic silver salt is at least 30% by mole and less than 80% by mole, and the binder has a glass transition temperature (Tg) of 45°C or higher.

[Claim 2] The photothermographic material according to claim 1, wherein a silver iodide content of the photosensitive silver halide is 5% by mole or more.

[Claim 3] The photothermographic material according to claim 1 or 2, wherein the silver iodide content of the photosensitive silver halide is 30% by mole or more.

[Claim 4] The photothermographic material according to claims 1 to 3, wherein the silver iodide content of the photosensitive silver halide is 70% by mole or more.

[Claim 5] The photothermographic material according to claims 1 to 4, wherein the silver iodide content of the photosensitive silver halide is 90% by mole or more.

[Claim 6] The photothermographic material according to claims 1 to 5, wherein an average grain size of the photosensitive silver halide is 5 nm to 80 nm.

[Claim 7] The photothermographic material according to claims 1 to 6, wherein the average grain size of the photosensitive silver halide is 10 nm to 55 nm.

[Claim 8] The photothermographic material according to claim 1 to 8, wherein the binder comprises polyvinyl butyral in an amount of 50% by mass or more.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Industrial Field of the Invention]

The present invention relates to a photothermographic material, and more particularly, to a photothermographic material that has a high sensitivity with a low degree of fogging while exhibiting excellent in dark stability.

[0002]

[Prior Art]

In the medical imaging field and the graphic arts field, there has been, in

recent years, a strong desire for a dry photographic process from the viewpoints of environmental conservation and space saving. Further, the development of digitization in these fields has resulted in the rapid development of systems in which image information is captured and stored in a computer, whereafter the image information is processed, if necessary, by the computer which outputs the image information through communication to a desired location, and the image information is further output, at the site, onto a photosensitive material using a laser image setter or a laser imager, followed by development thereof to form an image on the photosensitive material. It is required that the photosensitive material be able to record an image under exposure to a laser with a high intensity and that a clear black-tone image with a high resolution and sharpness can be formed. While various kinds of hard copy systems using a pigment or a dye such as an ink-jet printer or an electrophotographic system have been distributed as a general image forming system using such a digital imaging recording material, images in the digital imaging recording material obtained by such a general image forming system are insufficient in terms of image qualities required for medical images. To facilitate diagnosis, image qualities (such as sharpness, granularity, gradation, tone) and high recording speed (sensitivity) are required. However, digital imaging recording materials have not reached a level at which they can replace medical silver salt film processed by conventional wet development.

[0003]

On the other hand, thermographic systems using organic silver salts are known. (See patent documents 1 and 2, and non-patent document 1, for example). Generally, a photothermographic material, in particular, comprises an image

forming layer in which a photosensitive silver halide, a reducing agent, a reducible silver salt (for example, an organic silver salt) and if necessary, a toner controlling a color tone of developed silver are dispersed in a binder matrix.

[0004]

A black-toned silver image is formed in a photothermographic material by heating the photothermographic material to a high temperature (for example, 80°C or higher) after imagewise exposure to cause an oxidation-reduction reaction between the silver halide or the reducible silver salt (functioning as an oxidizing agent) and the reducing agent. The oxidation-reduction reaction is accelerated by a catalytic action of a latent image generated on the silver halide by exposure. As a result, a black-toned silver image is formed in an exposed region. Such a photothermographic material is disclosed in many patent documents (Patent Documents 3 and 4).

[0005]

On the other hand, a gas laser (Ar^+, He-Ne, or He-Cd), a YAG laser, a dye laser, a laser diode or the like is generally used as a laser beam. A laser diode and a second harmonic generation element or the like can also be used. With regard to an emitting wavelength, lasers in a wide wavelength range from the blue region to the infrared region are used. Among these, an infrared laser diode is particularly suitable for design of a laser image output system which is inexpensive and can obtain stable light emission, and which, in particular, is compact, excellent in operability, and not restricted with respect to an installation location. For this reason, the photothermographic material is required to have infrared sensitivity.

Various efforts have been made for enhancing infrared sensitivity. However, infrared spectrum sensitization has a problem in that it is generally unstable and decomposes during storage of the photosensitive material, leading to decrease in sensitivity, and there is an increased demand for improvement in preservation stability, together with increased sensitivity.

[0006]

Recently, a blue laser diode has been developed, enabling image recording with high precision, and stable output can be obtained with increased recording density and long life. Therefore, demand for the blue laser diode is expanding and a photothermographic recording material compatible with the blue laser diode is required.

[0007]

Since the above-described thermographic system using an organic silver salt has no fixing step, there has been a considerable problem in image stability after development, particularly with respect to worsening of print-out when exposed to light. As means for improving the print-out, a method in which silver iodide formed through conversion of an organic silver salt is employed is disclosed (see Patent Documents 5 and 6). There are provided other examples using silver iodide. However, in all of these, neither a sufficient sensitivity nor a sufficient fogging level is achieved, leading to a poor photosensitive material which is not suitable for practical use (see Patent Documents 7 and 8).

[0008]

There has been a demand for higher sensitivity in a photothermographic material using an organic silver salt, in order to increase an image recording speed, and there has also been a demand for reduced fogging to improve the capacity for medical diagnosis. Further, it is extremely important to improve dark stability of a thermally developed image in order for it to replace medical silver salt film processed by conventional wet development.

[0009]

[Patent document 1]

U.S. Patent No. 3152904

[Patent document 2]

U.S. Patent No. 3457075

[Patent document 3]

U.S. Patent No. 2910377

[Patent document 4]

Japanese Patent Application Publication (JP-B) No. 43-4924.

[Patent document 5]

U.S. Patent No. 6143488

[Patent document 6]

European Patent (EP) No. 0922995.

[Patent document 7]

JP-B No. 58-118639

[Patent document 8]

U.S. Patent No. 6274297

[Non-patent document]

Klosterboer, "Thermally Processed Silver Systems", in "Imaging Processes and Materials" coedited by J. Sturge, V. Walworth and A. Shepp, Neblette 8th Ed., Chapter 9, pp.279-291, 1989, the disclosures of which are incorporated by reference herein.

[0010]

[Means for Solving the Problems]

An object of the present invention is to improve image stability in resistance to darkness and heat after subjecting to a thermal development processingto by increasing sensitivity and by decreasing fogging of a conventional photothermographic material.

[0011]

[Problems to be Solved by the Invention]

The present inventors found out that the above-described problems can be solved by the followingmeans.

(1) A photothermographic material comprising, on a support, a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder, wherein the photothermographic material comprises a compound having a group adsorptive to silver halide and a reducible group or a precursor of the compound, a silver behenate content of the non-photosensitive organic silver salt is at least 30% by mole and less than 80% by mole, and the binder has a glass transition temperature (Tg) of 45°C or higher.

(2) The photothermographic material according to (1), wherein a silver iodide

content of the photosensitive silver halide is 5% by mole or more.

(3) The photothermographic material according to (1) or (2), wherein the silver iodide content of the photosensitive silver halide is 30% by mole or more.

(4) The photothermographic material according to (1) to (3), wherein the silver iodide content of the photosensitive silver halide is 70% by mole or more.

(5) The photothermographic material according to (1) to (4), wherein the silver iodide content of the photosensitive silver halide is 90% by mole or more.

(6) The photothermographic material according to (1) to (5), wherein an average grain size of the photosensitive silver halide is 5 nm to 80 nm.

(7) The photothermographic material according to (1) to (6), wherein the average grain size of the photosensitive silver halide is 10 nm to 55 nm.

(8) The photothermographic material according to (1) to (7), wherein the binder comprises polyvinyl butyral in an amount of 50% by mass or more.

[0012]

[Embodiments]

The invention provides a photothermographic material comprising, on a support, at least a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder, wherein the photothermographic material contains a compound having a group adsorptive to silver halide and a reducible group, or a precursor of the compound, a silver behenate content of the non-photosensitive organic silver salt isat least 30% by mole and less than 80% by mole, and the binder has a glass transition temperature (Tg) of 45°C or higher.

A detailed description of the photothermographic material according to the invention will be made, hereinafter.

[0013]

1. Compound having adsorptive group and reducible group

The photothermographic material of the present invention is characterized by comprising a compound having an adsorptive group and a reducible group in a molecule. It is preferred that the compound having an adsorptive group and a reducible group used in the invention is represented by the following formula (I).

[0014]

Formula (I) A-(W)n-B

[0015]

In formula (I), A represents a group capable of adsorption to a silver halide (hereafter, it is called an adsorptive group) and W represents a divalent connecting group and n represents 0 or 1 and B represents a reducible group.

[0016]

Next, formula (I) is explained in more detail.

In formula (I), the adsorptive group represented by A is a group to adsorb directly to a silver halide or a group to promote adsorption to a silver halide. As typical examples, a mercapto group (or the salt thereof), a thione group (-C(=S)-), a nitrogen atom, a heterocyclic ring containing at least one atom selected from a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom, a sulfide group, a disulfide group, a cationic group, an ethynyl group and the like are described.

[0017]

The mercapto group as an adsorptive group means a mercapto group (and the salt thereof) itself and simultaneously more preferably represents a heterocyclic ring group or an aryl group or an alkyl group substituted by at least one mercapto group (or the salt thereof). Herein, as the heterocyclic ring group, a monocyclic or a condensed aromatic or nonaromatic heterocyclic ring group having at least a 5 to 7 membered ring, e.g., an imidazole ring group, a thiazole ring group, an oxazole ring group, a benzimidazole ring group, a benzothiazole ring group, a benzoxazole ring group, a triazole ring group, a thiadiazole ring group, an oxadiazole ring group, a tetrazole ring group, a purine ring group, a pyridine ring group, a quinoline ring group, an isoquinoline ring group, a pyrimidine ring group, a triazine ring group and the like are described. A heterocyclic ring having quarternalized nitrogen atom may also be adopted, wherein a mercapto group as a substituent may dissociate to form a mesoion. As examples of such heterocyclic ring group, an imidazolium ring group, a pyrazolium ring group, a thiazolium ring group, a triazolium ring group, a tetrazolium ring group, a thiadiazolium ring group, a pyridinium ring group, a pyrimidinium ring group, a triazinium ring group and the like are described and among them, a triazolium ring group (e.g., a 1,2,4-triazolium-3-thiolate ring group) is preferable. As an aryl group, a phenyl group or a naphthyl group is described. As an alkyl group, a straight chain, branched chain or cyclic alkyl group having 1 to 30 carbon atoms is described. As a counter ion, whereby a mercapto group forms the salt thereof, a cation such as an alkali metal, an alkali earth metal, a heavy metal and the like (Li^+, Na^+, K^+, Mg^{2+}, Ag^+, Zn^{2+} and the like), an

ammonium ion, a heterocyclic ring group having quaternalized nitrogen atom, a phosphonium ion and the like are described.

[0018]

Further, the mercapto group as an adsorptive group may become a thione group by a tautomerization. For example, a thioamide group (herein –C(=S)-NH- group) and the group containing the said thioaminde group as a partial structure, namely a chain or a cyclic thioamide, thioureide, thiourethane or dithiocarbanic ester group and the like are described. Herein, as cyclic examples, a thiazolidine-2-thione group, an oxazolidine-2-thione group, a 2-thiohydantoin group, a rhodanine group, an isorhodanine group, a thiobarbituric acid group, a 2-thioxo-oxazolidine-4-one group and the like are described.

[0019]

The thione group as an adsorptive group may also contain a chain or a cyclic thioamide group, a thioureido group, a thiouretane group or a thioester group which can not tautomerize to a mercapto group (having no hydrogen atom on the α-position of a thione group) with containing a mercapto group capable to become a thion group by tautomerization.

[0020]

The heterocyclic ring group containing at least one atom selected from a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom represents a nitrogen atom containing heterocyclic ring group having –NH- group, as a partial structure of hetero ring, capable to form a silver iminate (>NAg) or a heterocyclic

ring group, having –S- group, -Se- group, -Te- group or =N- group as a partial structure of hetero ring, and capable to coordinate to a silver ion by a chelate bonding. As the former examples, a benzotriazole group, a triazole group, an indazole group, a pyrazole group, a tetrazole group, a benzimidazole group, a purine group and the like are described. As the latter examples, a thiophene group, a thiazole group, a benzoxazole group, a thiadiazole group, an oxadiazole group, a triazine group, a selenoazole group, a benzoselenazole group, a tellurazole group, a benzotellurazole group and the like are described. The former is preferable.

[0021]

The sulfide group or disulfide group as an adsorptive group contains all groups having "–S-"or"–S-S-"as a partial structure, but the group having "alkyl (or an alkylene)-X-alkyl (or alkylene) ", "aryl (or arylene)–X- alkyl (or alkylene) ", and "aryl (or arylene)-X- aryl (or arylene) "as a partial structure are preferably, wherein X represents "–S- group" or "–S-S- group". Further, these sulfide groups or disulfide groups may form a cyclic structure. As typical examples of a cyclic structure formation, the group containing a thiorane ring, a 1,3-dithiorane ring, a 1,2-dithiorane ring, a thiane ring, a dithiane ring, a thiomorphorine ring and the like are described. As a sulfide group, the group having " alkyl (or alkylene)-S-alkyl (or alkylene)" as a partial structure and as a disulfide group, a 1,2-dithiorane ring group are particularly preferably described.

[0022]

The cationic group as an adsorptive group means the group containing a

quaternalized nitrogen atom, such as an ammonio group or a nitrogen containing heterocyclic ring group containing a quaternalized nitrogen atom. Herein, an ammonio group means a trialkylammonio group, a dialkylarylammonio group, an alkyldiarylammonio group, such as a benzyldimethylammonio group, a trihexylammonio group, a phenyldiethylammonio group and the like are described. As examples of the heterocyclic ring group containing a quaternalized nitrogen atom, a pyridinio group, a quinolinio group, an isoquinolinio group, an imidazolio group and the like are described. A pyridinio group and an imidazolio group are preferable and a pyridinio group is particularly preferable. These nitrogen containing heterocyclic ring groups containing a quaternalized nitrogen atom may have any substituent, but in the case of a pyridinio group and an imidazolio group, an alkyl group, an aryl group, an acylamino group, a chlorine atom, an alkoxycarbonyl group, a carbamoyl group and the like are preferably as a substituent and in a pyridinio group, a phenyl group is particularly preferable as a substituent.

[0023]

The ethynyl group as an adsorptive group means $-C\equiv CH$ group and the said hydrogen atom may be substituted.

[0024]

The adsorptive group described above may have any substituent. As examples of a substituent, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom or an iodine atom), an alkyl group (a straight chain alkyl group, a branched chain alkyl group, a cyclic alkyl group and a bicyclic alkyl group and an

active methine group are contained), an alkenyl group, an alkynyl group, an aryl group, a heterocyclic ring group (irrelevant to a substituting position), an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic oxycarbonyl ring group, a carbamoyl group, a N-hydroxycarbamoyl group, a N-acylcarbamoyl group, a N-sulfonylcarbamoyl group, a N-carbamoylcarbamoyl group, a thiocarbamoyl group, a N-sulfamoylcarbamoyl group, a carbazoyl group, a carboxy group or a salt thereof, an oxalyl group, an oxamoyl group, a cyano group, a carbonimidoyl group, a formyl group, a hydroxy group, an alkoxy group (a group containing an ethyleneoxy group or a propyleneoxy group as repeating unit is contained), an aryloxy group, an oxy group substituted to heterocyclic ring, an acyloxy group, (an alkoxy or an aryloxy)carbonyloxy group, a carbamoyloxy group, a sulfonyloxy group, an amino group, (an alkyl, an aryl or a heterocyclic ring)amino group, an acylamino group, a sulfonamide group, an ureido group, a thioureido group, a N-hydroxyureido group, an imide group, (an alkoxy or aryloxy)carbonylamino group, a sulfamoylamino group, a semicarbazide group, a thiosemicarbazide group, a hydrazino group, an ammonio group, an oxamoylamino group, a N-(alkyl or aryl)sulfonylureido group, a N-acylureido group, a N-acylsulfamoylamino group, a hydroxyamino group, a nitro group, a heterocyclic ring group containing quaternalized nitrogen atom (e.g., a pyridinio group, an imidazolio group, a quinolinio group, an isoquinolinio group), an isocyano group, an imino group, a mercapto group, (an alkyl, an aryl or a heterocyclic ring)thio group, (an alkyl, an aryl or a heterocyclic ring)dithio group, (an alkyl, or an aryl)sulfonyl group, (an alkyl or an aryl)sulfinyl group, a sulfo group and the salt thereof, a sulfamoyl group, a N-acylsulfamoyl group, a N-sulfonylsulfamoyl group and a salt thereof, a phosphino group, a phosphinyl group, a phosphinyloxy group,

a phosphinylamino group, a silyl group and the like are described. Herein, the active methine group means a mathine group subsutituted by two electron-withdrawing group, wherein the electron-withdrawing group means an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfamoyl group, a trifluoromethyl group, a cyano group, a nitro group and a carbonimidoyl group. Herein, two electron-withdrawing groups may bind each other to form a cyclic structure. The salt means a cation such as from an alkali metal, an alkali earth metal and a heavy metal and an organic cation such as an ammonium ion, a phosphonium ion and the like.

[0025]

Further, as typical examples of an adsorptive group, the compounds described in pages 4 to 7 in the specification of JP-A No.11-95355 are described.

[0026]

As an adsorptive group represented by A in general formula (I), a heterocyclic ring group substituted by a mercapto group (e.g., a 2-mercaptothiadiazole group, a 3-mercapto-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercapto-1,3,4-oxadiazole group, a 2-mercaptobenzothiazole group, a 2-mercaptobenzimidazole group, a 1,5-dimethyl-1,2,4-triazorium-3-thiolate group and the like), a heterocyclic ring group substituted by two mercapto groups (e.g., a 2,4-dimercaptopyrimidine group, a 2,4-dimercatotriazine group, a 3,5-dimercapto-1,2,4-triazole group, a 2,5-dimercapto-1,3-thiazole group and the like) or a nitrogen atom containing heterocyclic ring

group having a –NH- group capable to form an imino-silver (>NAg) as a partial structure of heterocyclic ring (e.g., a benzotriazole group, a benzimidazole group, an indazole group and the like) are more preferably and a heterocyclic ring group substituted by two mercapto groups is particularly preferable.

[0027]

In formula (I), W represents a divalent connection group. The said connection group may be any divalent connection group, as far as it does not give a bad effect toward a photographic property. For example, a divalent connection group composed of a carbon atom, a hydrogen atom, an oxygen atom a nitrogen atom and a sulfur atom can be used. As typical examples, an alkylene group having 1 to 20 carbon atoms (e.g., a methylene group, an ethylene group, a trimethylene group, a tetramethylene group, a hexamethylene group and the like), an arylene group having 6 to 20 carbon atoms (e.g., a phenylene group, a nephthylene group and the like), $-CONR_1-$, $-SO_2NR_2-$, -O-, -S-, $-NR_3-$, $-NR_4CO-$, $-NR_5SO_2-$, $-NR_6CONR_7-$, -COO-, -OCO- and the combination of these connecting groups are described. Herein, R_1, R_2, R_3, R_4, R_5, R_6 and R_7 independently represent a hydrogen atom, an aliphatic group and an aryl group. As preferred aliphatic group represented by R_1, R_2, R_3, R_4, R_5, R_6 and R_7, a straight chain, branched chain or cyclic alkyl group, an alkenyl group, an alkynyl group, an aralkyl group having 1 to 30 carbon atoms, particularly 1 to 20 carbon atoms (e.g., a methyl group, an ethyl group, an isopropyl group, a t-butyl group, a n-octyl group, a n-decyl group, a n-hexadecyl group, a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, an aryl group, a 2-butenyl group, a 3-pentenyl group, a propargyl group, a 3-pentynyl group, a benzyl group and the like) are described.

In formula (I), as an aryl group represented by R_1, R_2, R_3, R_4, R_5, R_6 and R_7, a monocyclic or condensed ring aryl group having 6 to 30 carbon atoms is preferable and that having 6 to 20 carbon atoms is more preferable. For example, a phenyl group and a naphthyl group and the like are described. The above substituent represented by R_1, R_2, R_3, R_4, R_5, R_6 and R_7 may have still more any substituent, whereby the substituent defined as similar to the substituent for an adsorptive group described above.

[0028]

In formula (I), a reducible group represented by B represents the group capable to reduce a silver ion. As the examples, a formyl group, an amino group, a triple bond group such as an acetylene group, a propargyl group and the like, an alkylmercapto group or an arylmercapto group, hydroxylamines, hydroxamic acids, hydroxyureas, hydroxyurethanes, hydroxysemicarbazides, reductones (reductone derivatives are contained), anilines, phenols (chroman-6-ols, 2,3-dihydrobenzofuran-5-ols, aminophenols, sulfonamidophenols and polyphenols such as hydroquinones, catechols, resorcinols, benzenetriols, bisphenols are contained), hydrazines, hydrazides and phenidones can be described.

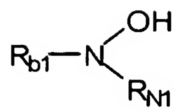
[0029]

In formula (I), a preferable reducible group represented by B is the residue derived from the compound represented by general fomulae B_1 to B_{13}.

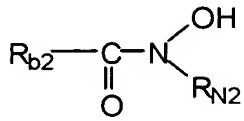
[0030]

[F1]

(B_1)



(B_2)



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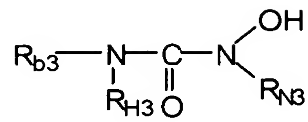

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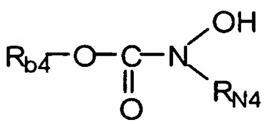

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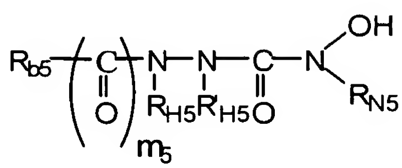

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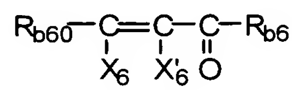

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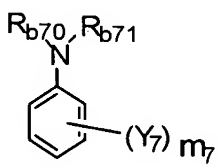

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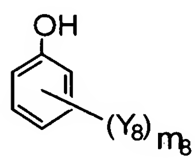

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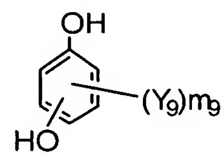

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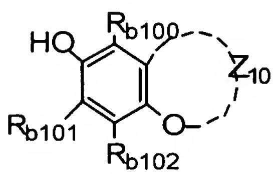

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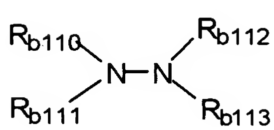

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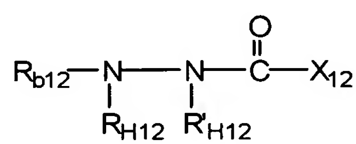

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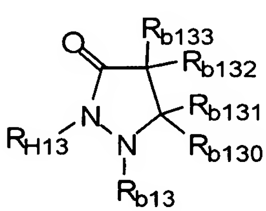


[0031]

In formulae (B_1) to (B_{13}), R_{b1}, R_{b2}, R_{b3}, R_{b4}, R_{b5}, R_{b70}, R_{b71}, R_{b110}, R_{b111}, R_{b112}, R_{b113}, R_{b12}, R_{b13}, R_{N1}, R_{N2}, R_{N3}, R_{N4}, and R_{N5} represent a hydrogen atom, an alkyl group, an aryl group or a heterocyclic ring group; and R_{H3}, R_{H5}, R'_{H5}, R_{H12}, R'_{H12}, and R_{H13} represent a hydrogen atom, an alkyl group, an aryl group, an acyl group, an alkylsulfonyl group or an arylsulfonyl group; and among them, R_{H3} may still more represent a hydroxy group. R_{b100}, R_{b101}, R'_{b102}, and R_{b130} to R_{b133} represent a hydrogen atom or a substituent. Y_7 and Y_8 represent a substituent except for a hydroxy group and Y_9 represents a substituent and m_5 represents 0 or 1 and m_7 represents an integer from 0 to 5 and m_8 represents an integer from 1 to 5 and m_9 represents an integer from 0 to 4. Y_7, Y_8 and Y_9 may still more represent an aryl group condensed to a benzene ring (e.g., a benzene condensed ring) and further more may have a substituent. Z_{10} represents a non-metal atomic group capable to form a ring and X12 represents a hydrogen atom, an alkyl group, an aryl group, a heterocyclic ring group, an alkoxy group, an amino group (an alkylamino group, an arylamino group, an amino group substituted to a heterocyclic ring or a cyclic amino group are contained) and a carbamoyl group.

In formula (B_6), X_6 and X'_6 each represent a hydroxy group, an alkoxy group, a mercapto group, an alkylthio group, an amino group (an alkylamino group, an arylamino group, an amino group substituted to a heterocyclic ring group or a cyclic amino group are contained), an acylamino group, a sulfonamide group, an alkoxycarbonylamino group, an ureido group, an acyloxy group, an acylthio group, an alkylaminocarbonyloxy group or an arylaminocarbonyloxy group. R_{b60} and R_{b61} represent an alkyl group, an aryl group, an amino group, an alkoxy group and an aryloxy group and R_{b60} and R_{b61} may bind each other to form a cyclic structure.

[0032]

In the explanation of each group in above formula (B_1) to (B_{13}), an alkyl group means a straight chain, branched chain or cyclic and a substituted or unsubstituted alkyl group having 1 to 30 carbon atoms and an aryl group means a monocyclic or condensed and a substituted or unsubstituted aromatic alicyclic ring such as a phenyl group and a naphthyl group and a heterocyclic ring group means an aromatic or nonaromatic and a monocyclic or condensed and a substituted or unsubstituted heterocyclic ring group having at least one hetero atom.

And the substituent described in the explanation of each substituent in formula (B_1) to (B_{13}) means the same as the substituent for an adsorptive group described above. These substituents may be more substituted by these substituents.

[0033]

In formula (B_1) to (B_5), R_{N1}, R_{N2}, R_{N3}, R_{N4} and R_{N5} are preferably a hydrogen atom or an alkyl group and herein, an alkyl group is preferably a straight, branched or cyclic and a substituted or unsubstituted alkyl group having 1 to 12 carbon atoms and more preferably a straight, branched or cyclic and a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms such as a methyl group, an ethyl group, a propyl group, a benzyl group and the like.

[0034]

In formula (B_1), R_{b1} is preferably an alkyl group and a heterocyclic ring group and herein, an alkyl group means a straight, branched or cyclic and a

substituted or unsubstituted alkyl group and is preferably an alkyl group having 1 to 30 carbon atoms and more preferably an alkyl group having 1 to 8 carbon atoms. A heterocyclic ring group means a 5 or 6 membered monocyclic or condensed ring and an aromatic or nonaromatic heterocyclic ring group and may have a substituent. As a heterocyclic ring group, an aromatic heterocyclic ring group is preferable, for examples, a pyridine ring group, a pyrimidine ring group, a triazine ring group, a thiazole ring group, a benzothiazole ring group, an oxazole ring group, a benzoxazole ring group, an imidazole ring group, a benzimidazole ring group, a pyrazole ring group, an indazole ring group, an indole ring group, a purine ring group, a quinoline ring group, an isoquinoline ring group, a quinazoline ring group and the like are described. Especially, a triazine ring group and a benzothiazole ring group are preferable. The case, wherein an alkyl group or a heterocyclic ring group represented by R_{b1} further has one or two or more of $-NH(R_{N1})OH$ group as its substituent is one of preferred embodiments of the compound represented by formula (B1).

[0035]

In formula (B_2), R_{b2} is preferably an alkyl group, an aryl group or a heterocyclic ring group and more preferably is an alkyl group or an aryl group. Preferred range of alkyl group is similar to that in the explanation of R_{b1}. As an aryl group, a phenyl group or a naphthyl group is preferable and a phenyl group is particularly preferable and may have a substituent. The case, wherein the group represented by R_{b2} further has one or two or more of $-NH(R_{N2})OH$ group as its substituent is one of preferred embodiments of the compound represented by formula (B_2).

[0036]

In formula (B_3), R_{b3} is preferably an alkyl group or an aryl group, wherein a preferred range thereof is similar to that in the explanation of R_{b1} and R_{b2}. R_{H3} is preferably a hydrogen atom, an alkyl group or a hydroxy group and more preferably a hydrogen atom. The case, wherein the group represented by R_{b3} further has one or two or more of $-NH(R_{N3})CON(R_{N3})OH$ group as its substituent is one of preferred embodiments of the compound represented by formula (B3). And R_{b3} and R_{N3} may bind each other to form a cyclic structure (preferably a 5 or 6 membered saturated heterocyclic ring).

[0037]

In formula (B4), R_{b4} is preferably an alkyl group, wherein a preferred range thereof is similar to that in the explanation of R_{b1}. The case where the group represented by R_{b4} further has one or two or more of $-OCON(R_{N4})OH$ group as its substituent is one of preferred embodiments of the compound represented by formula (B4).

[0038]

In formula (B5), R_{b5} preferably is an alkyl group or an aryl group and more preferably is an aryl group, wherein a preferred range is similar to that in the explanation of R_{b1} and R_{b2}. R_{H5} and R'_{H5} are preferably a hydrogen atom or an alkyl group and more preferably a hydrogen atom.

[0039]

In formula (B_6), it is preferred that R_{b60} and R_{b61} bind each other to form a cyclic structure. The cyclic structure formed herein is 5 to 7 membered nonaromatic carbon ring or a heterocyclic ring and may be monocyclic or condensed ring. As typical examples of preferred cyclic structure, a 2-cyclopentene-1-one ring, a 2,5-dihydrofurane-2-one ring, a 3-pyrroline-2-one ring, a 4-pyrazoline-3-one ring, a 2-cyclohexene-1-one ring, a 4-pyrazoline-3-one ring, a 2-cyclohexene-1-one ring, a 5,6-dihydro-2H-pyrane-2-one ring, a 5,6-dihydro-2-pyridone ring, a 1,2-dihydronaphthalene-2-one ring, a cumarin ring (a benzo-α-pyrane-2-one ring), a 2-quinolone ring, a 1,4-dihydronaphthalene-1-one ring, a chromone ring (a benzo-γ-pyrane-4-one ring), a 4-quinolone ring, an indene-1-one ring, a 3-pyrroline-2,4-dione ring, an uracil ring, a thiouracil ring, a dithiouracil ring and the like are described and a 2-cycolopentene-1-one ring, a 2,5-dihydrofurane-2-one ring, 3-pyrroline-2-one ring, a 4-pyrazoline-3-one ring, a 1,2-dihydronaphthalene-2-one ring, a cumarin ring (a benzo-α-pyrane-2-one ring), a 2-quinolone ring, a 1,4-dihydronaphthalene-1-one ring, a chromone ring (a benzo-γ-pyrane-4-one ring), a 4-quinolone ring, an indene-1-one ring, a dithiouracil ring and the like are more preferably and a 2-cycolopentene-1-one ring, a 2,5-dihydrofurane-2-one ring, a 3-pyrroline-2-one ring, an indene-1-one ring and a 4-pyrazoline-3-one ring are still more preferable.

[0040]

When X_6 and X'_6 represent a cyclic amino group, a cyclic amino group means a nonaromatic nitrogen atom containing heterocyclic ring group bound at a nitrogen atom, e.g., a pyrrolidino group, a pyperidino group, a pyperadino group, a morphorino group, a 1,4-thiazine-4-yl group, a 2,3,5,6-tetrahydro-1,4-thiazine-4-yl

group, an indolyl group and the like are included.

[0041]

As X_6 and X'_6, a hydroxy group, a mercapto group, an amino group (an alkylamino group, an arylamino group or a cyclic amino group are contained), an acylamino group, a sulfonamide group, or an acyloxy group and an acylthio group are preferable and a hydroxy group, a mercapto group, an amino group, an alkylamino group, a cyclic amino group, a sulfonamide group, an acylamino group or an acyloxy group are more preferable and a hydroxy group, an amino group, an alkylamino group and a cyclic amino group are particularly preferable. Further, it is preferred that at least one of X_6 and X'_6 is a hydroxy group.

[0042]

In formula (B_7), R_{b70} and R_{b71} preferably are a hydrogen atom, an alkyl group or an aryl group and more preferably an alkyl group. The preferred range of alkyl group is similar to that in the explanation of R_{b1}. R_{b70} and R_{b71} may bind each other to form a cyclic structure (e.g., a pyrrolidine ring, a pyperidine ring, a morphorino ring, a thiomorphorino ring and the like). As the substituent represented by Y_7, an alkyl group (that preferred range is the same as the explanation of R_{b1}), an alkoxy group, an amino group, an acylamino group, a sulfonamide group, an ureido group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a chlorine atom, a sulfo group or the salt thereof, a carboxy group or the salt thereof and the like are preferable and m_7 preferably represents integer from 0 to 2.

[0043]

In formula (B_8), m_8 preferably is integer from 1 to 4 and the plural Y_8 may be same or different. Y_8 in the case, wherein m_8 is 1 or at least one of the plural Y_8 in the case, wherein m_8 is 2 or more, is preferably an amino group (an alkylamino group and an arylamino group are contained), a sulfonamide group or an acylamino group. In the case, wherein m_8 is 2 or more, remaining Y_8 is preferably a sulfonamide group, an acylamino group, an ureido group, an alkyl group, an alkylthio group, an acyl group, an alkoxycarbonyl group a carbamoyl group, a sulfo group or the salt thereof, a carboxy group or the salt thereof, a chlorine atom and the like. Herein, in the case, wherein o'-(or p'-)hydroxyphenylmethyl group (may have more substituents) is substituted at the ortho or para position toward a hydroxy group as the substituent represented by Y_8, these compounds represent a compound group generally called as a bisphenol. The said compound is one of the preferred examples represented by formula (B_8) too. Further, the case, wherein Y_8 represent a benzene condensed ring and results to represent naphthols for formula (B_8) is very preferable.

[0044]

In formula (B_9), the substitution position of two hydroxy groups may be each other an ortho position (catechols), a meta position (resorcinols) or a para position (hydroquinones). m_9 is preferably 1 or 2 and the plural Y_9 may be the same or different. As preferred substituents represented by Y_9, a chlorine atom, an acylamino group, an ureido group, a sulfonamide group, an alkyl group, an alkylthio group, an alkoxy group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a sulfo group or the salt thereof, a carboxy group or the salt

thereof, a hydroxy group, an alkylsulfonyl group, an arylsulfonyl group and the like are described. The case where Y_9 represents a benzene condensed ring and results to represent 1,4-naphthohydroquinones for formula (B_9) is also preferable. When formula (B_9) represents catechols, Y_9 is particularly preferably a sulfo group or the salt thereof and a hydroxy group.

[0045]

In formula (B_{10}), when R_{b100}, R_{b101} and R_{b102} represent substituents, preferred examples of substituent are similar to that in preferred examples of Y_9. Among them, an alkyl group (particularly a methyl group) is preferable. As preferred examples of a cyclic structure to form Z_{10}, are a chroman ring and a 2,3-dihydrobenzofurane ring are described and these cyclic structures may have a substituent and may form a spiro ring.

[0046]

In formula (B_{11}), as preferred examples of R_{b111}, R_{b112} and R_{b113} are an alkyl group, an aryl group or a heterocyclic ring group and their preferred ranges are similar to that in the explanation of R_{b1} and R_{b2}. Among them, an alkyl group is preferable and two alkyl groups in Rb_{110} to Rb_{113} may bind to form a cyclic structure. Herein, a cyclic structure means 5 to 7 membered nonaromatic heterocyclic ring, e.g., a pyrrolidine ring, a pyperidine ring, a morphorino group, a thiomorphorino group, a hexahydropyridazine ring and the like.

[0047]

In formula (B_{12}), R_{b12} preferably is an alkyl group, an aryl group or a

heterocyclic ring group and their preferred ranges are similar to that in the explanation of R_{b1} and R_{b2}. X_{12} preferably is an alkyl group, an aryl group (particularly a phenyl group), a heterocyclic ring group, an alkoxy group, an amino group (an alkylamino group, an arylamino group, an amino group sunstitiuted to a heterocyclic ring or a cyclic amino group are contained), and a carbamoyl group and more preferably is an alkyl group (particularly, an alkyl group having 1 to 8 carbon atoms is preferable), an aryl group (particularly, a phenyl group is preferable), an amino group (an alkylamino group, an arylamino group or a cyclic amino group are contained). R_{H12} and R'_{H12}, preferably are a hydrogen atom or an alkyl group and more preferably are a hydrogen atom.

[0048]

In formula (B_{13}), R_{b13} preferably is an alkyl group or an aryl group and their preferred ranges are similar to that in the explanation of R_{b1} and R_{b2}. R_{b130}, R_{b131}, R_{b132} and R_{b133} preferably are a hydrogen atom, an alkyl group (particularly, an alkyl group having 1 to 8 carbon atoms are preferable) and an aryl group (particularly, a phenyl group is preferable). R_{H13} preferably is a hydrogen atom or an acyl group and more preferably is a hydrogen atom.

[0049]

In formula (I), a reducible group represented by B preferably is hydroxylamines, hydroxamic acids, hydroxyureas, hydroxysemicarbazides, phenols, hydrazines, hydrazides and phenidones and more preferably is hydroxyureas, hydroxysemicarbazides, phenols, hydrazides and phenidones.

[0050]

The oxidation potential of a reducible group represented by B in formula (I), can be measured by using the measuring method described in Akira Fujishima, "DENKIKAGAKU SOKUTEIHO", pages 150 to 208, GIHODO SHUPPAN and NIHON KAGAKUKAI, "ZIKKEN KAGAKUKOUZA", 4th ed., vol. 9, pages 282 to 344, MARUZEN. For example, the method of rotating disc voltammetry can be used; namely the sample is dissolved in the solution (methanol : pH 6.5 Britton-Robinson buffer = 10% : 90% (% by volume)) and after bubbling with nitrogen gas during 10 minutes the voltamograph can be measured under the condition of 1000 rotations/minute, the sweep rate 20 mV/second, at 25°C by using a rotating disc electrode (RDE) made by glassy carbon as a working electrode, a platinum electrode as a counter electrode and a saturated calomel electrode as a reference electrode. The half wave potential (E1/2) can be calculated by that obtained voltamograph.

[0051]

When a reducible group represented by B in the present invention is measured by the method described above, an oxidation potential preferably is in the range of about -0.3 V to about 1.0 V, more preferably about -0.1 V to about 0.8 V, and most preferably about 0 V to about 0.7 V.

[0052]

Most of the reducible groups represented by B in the present invention are known in the photographic industry and those examples are described in the following patents. For example, JP-A Nos. 2001-42466, 8-114884, 8-314051, 8-

333325, 9-133983, 11-282117, 10-246931, 10-90819, 9-54384, 10-171060 and 7-77783 can be described. And as an example of phenols, the compound described in U.S. Patent No. 6054260 is described too.

[0053]

The compound of formula (I) in the present invention may have the ballasted group or polymer chain in it generally used in the nonmoving photographic additives as a coupler. And as a polymer, for example, the polymer described in JP-A No. 1-100530 can be described.

[0054]

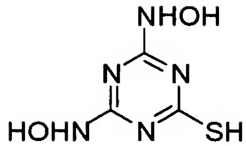
The compound of formula (I) in the present invention may be bis or tris type of compound. The molecular weight of the compound represented by formula (I) in the present invention is preferably 100 to 10000 and more preferably 120 to 1000 and particularly preferably 150 to 500.

[0055]

The examples of the compound represented by formula (I) in the present invention are shown below, but the present invention is not limited in these. The compounds shown in JP-A Nos. 2000-330247 and 2001-42446 are also preferable examples.

[0056]

[F2]



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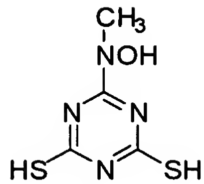

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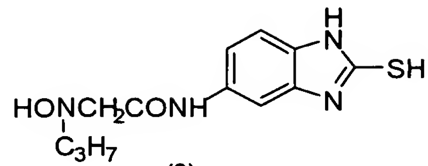

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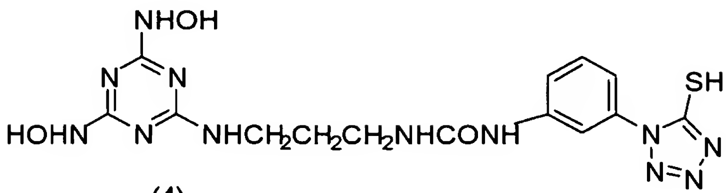

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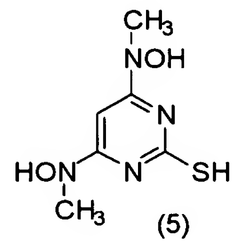

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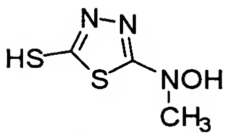

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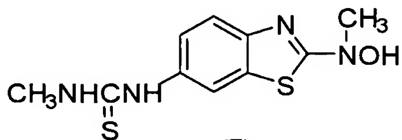

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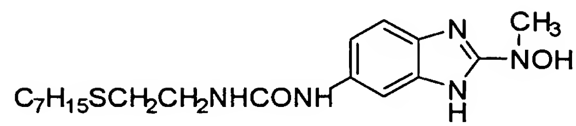

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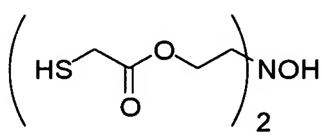

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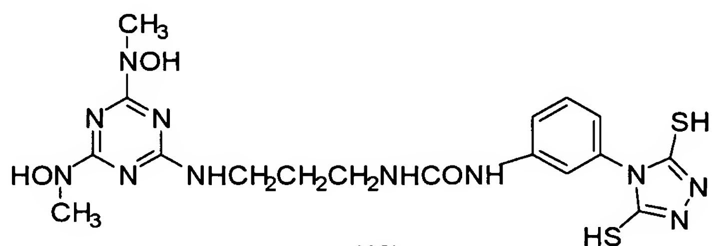

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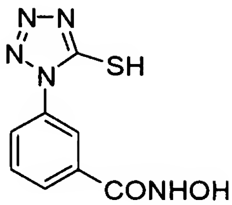
[0057]

[F3]



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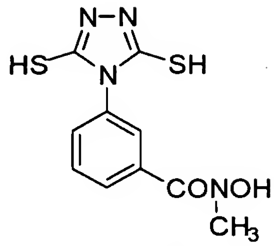

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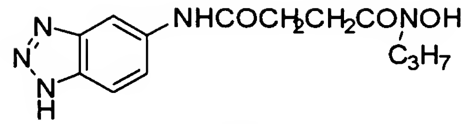

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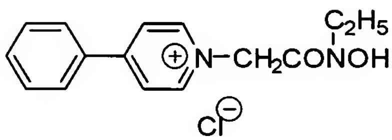

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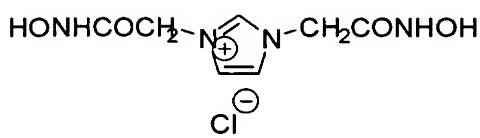

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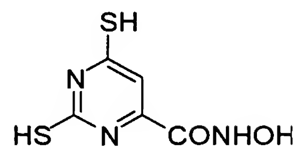

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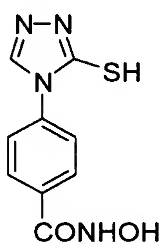

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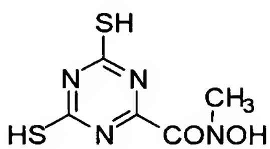

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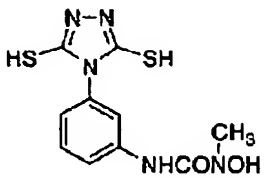
[0058]

[F4]



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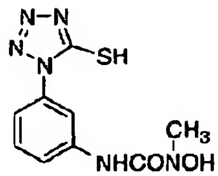

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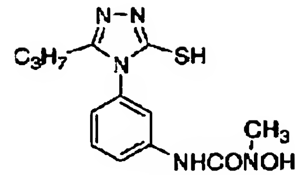

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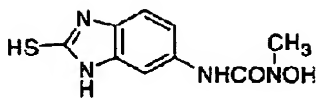

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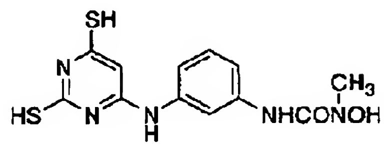

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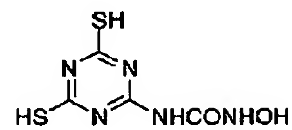

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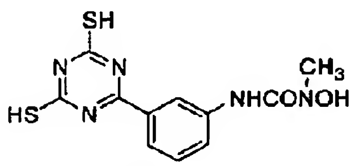

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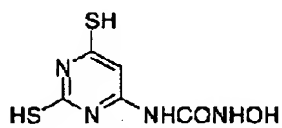

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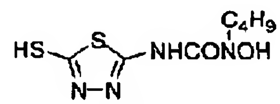

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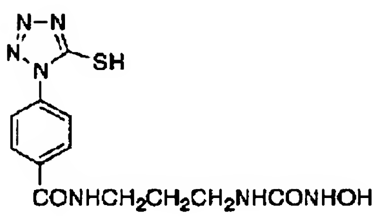

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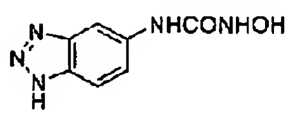

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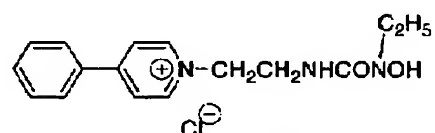

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[0059]

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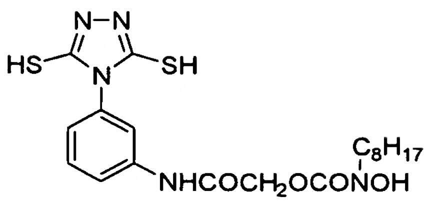

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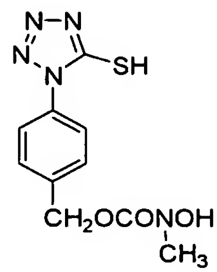

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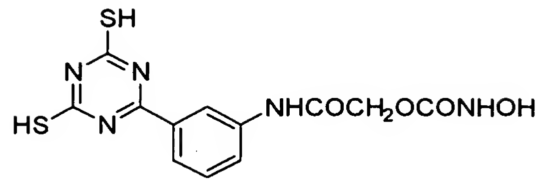

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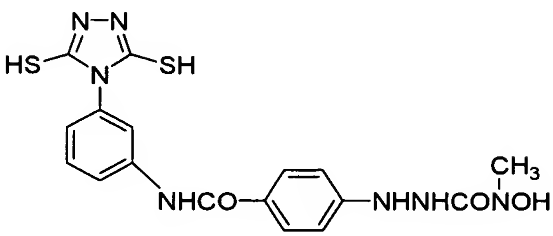

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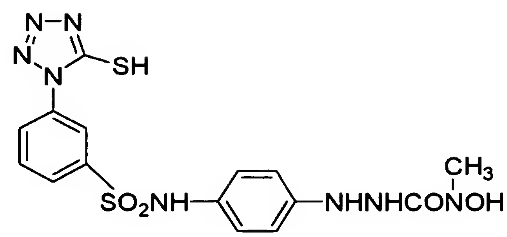

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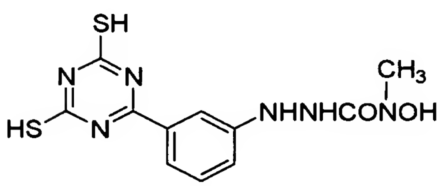

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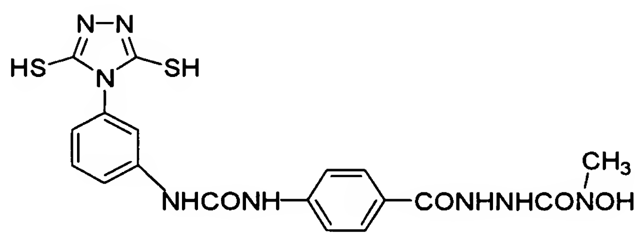

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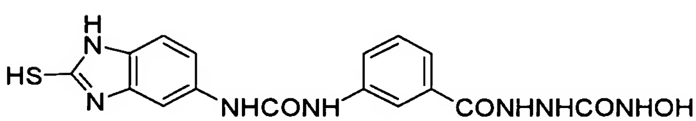

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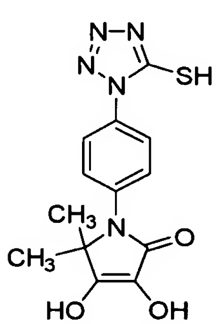

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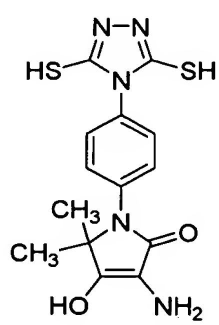

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[0060]

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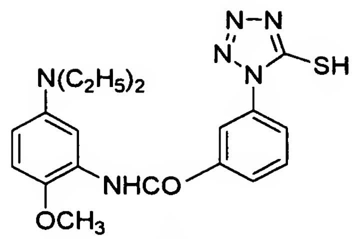

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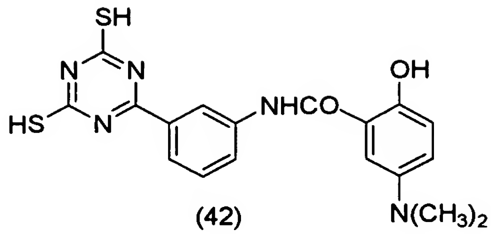

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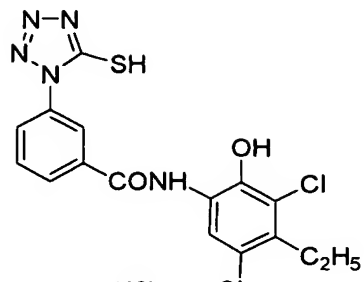

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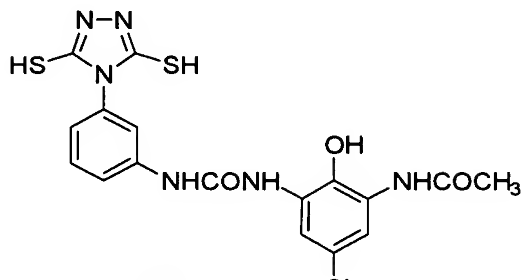

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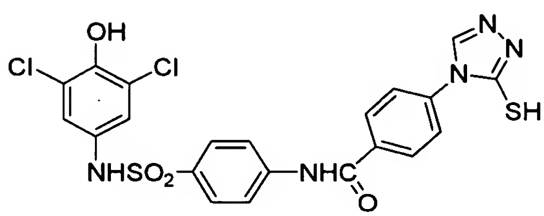

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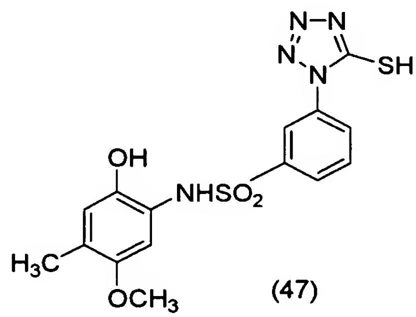

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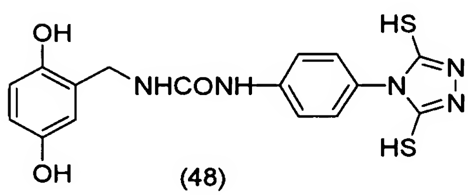

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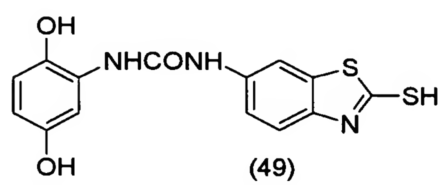

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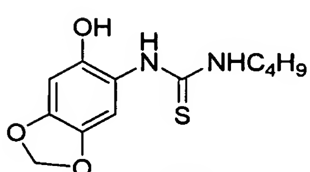

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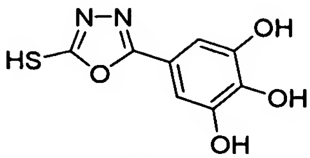
[0061]

[F7]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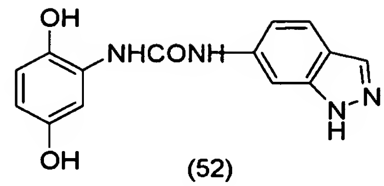
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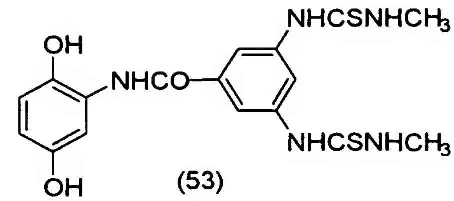
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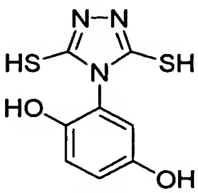
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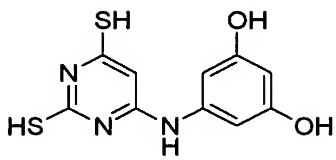
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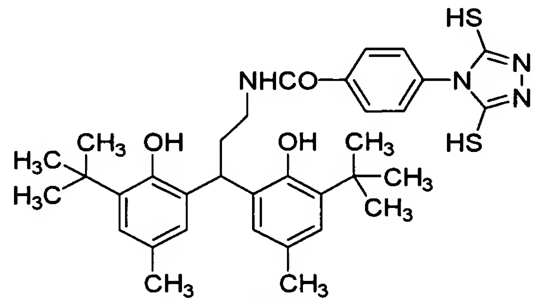
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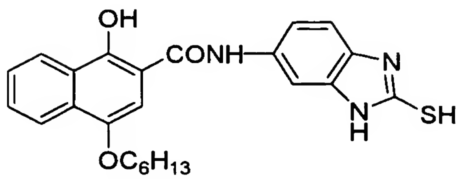
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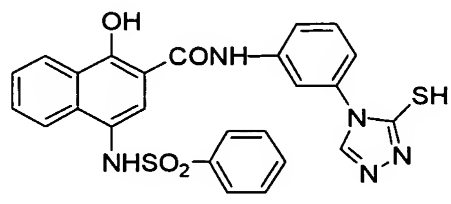
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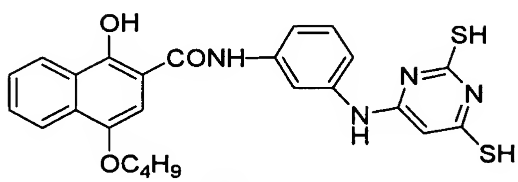
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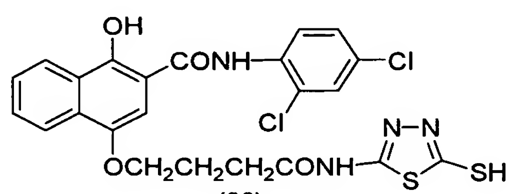
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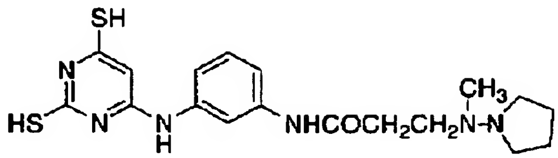

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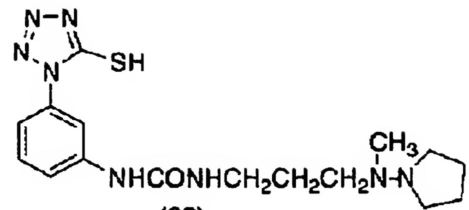

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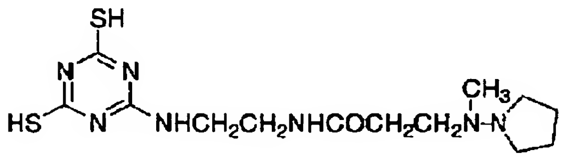

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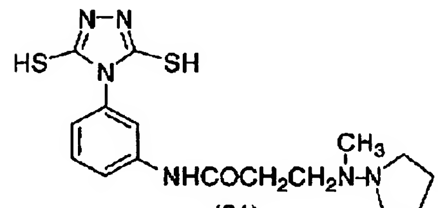

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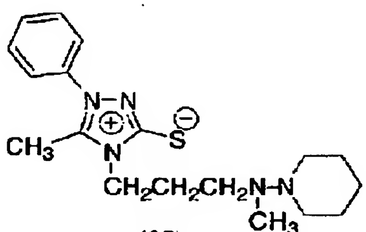

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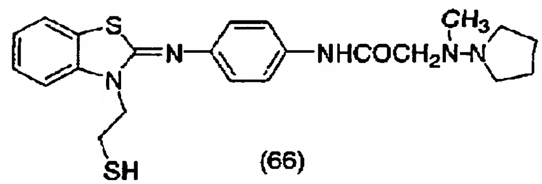

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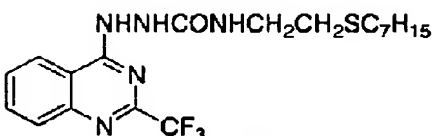

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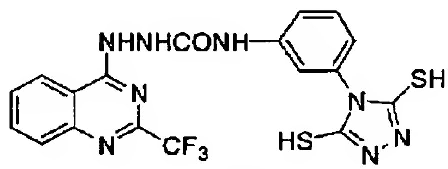

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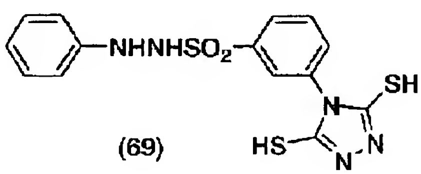

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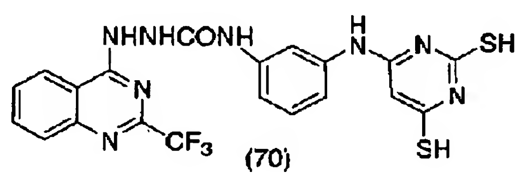

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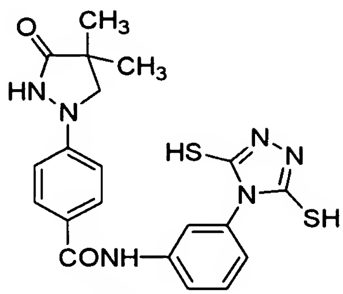

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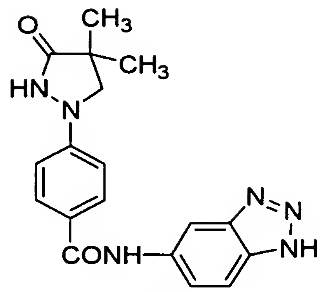

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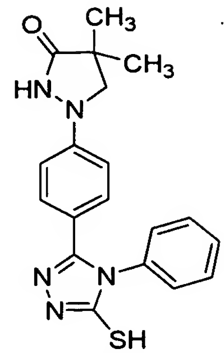

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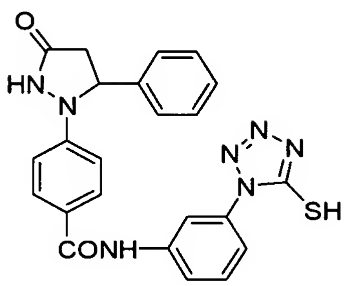

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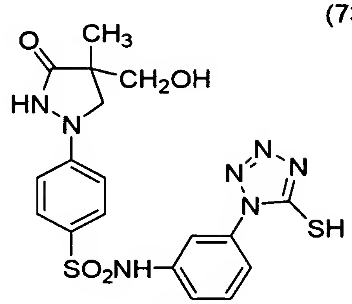

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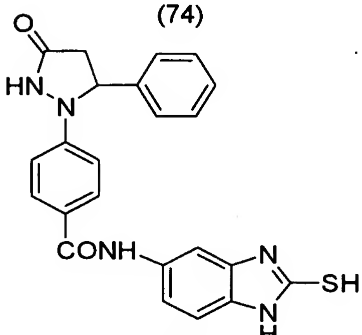

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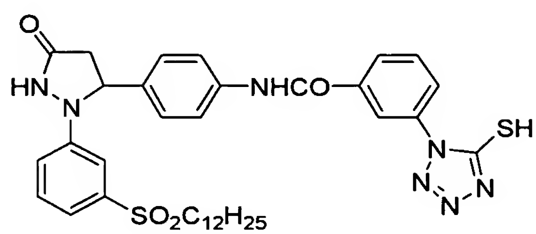

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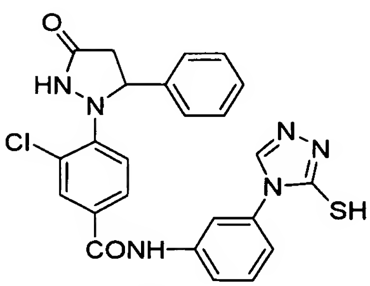

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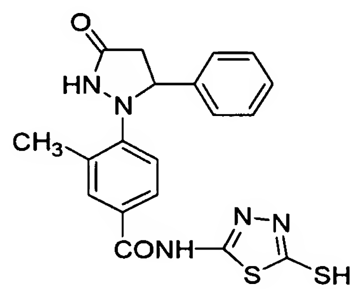

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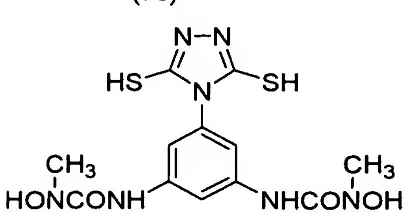

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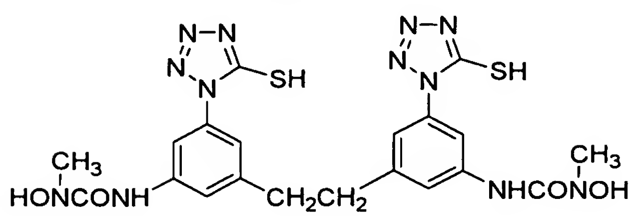

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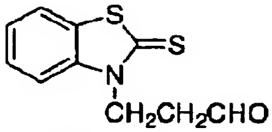

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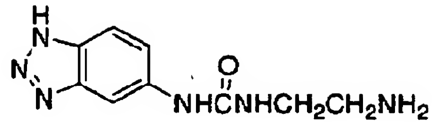

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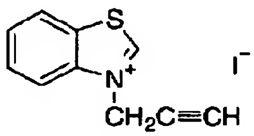

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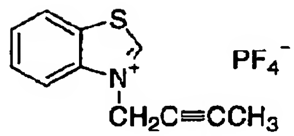

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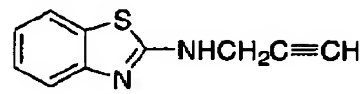

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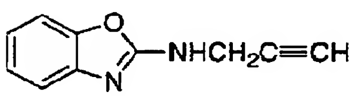

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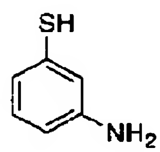

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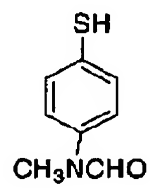

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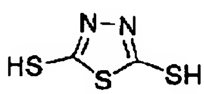

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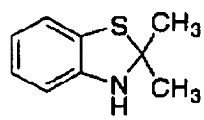

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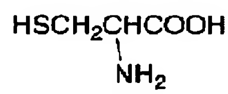

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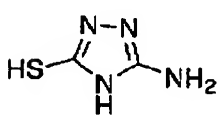

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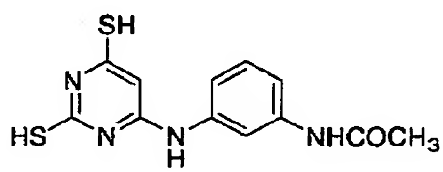

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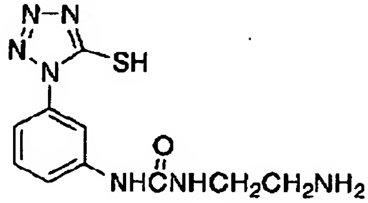

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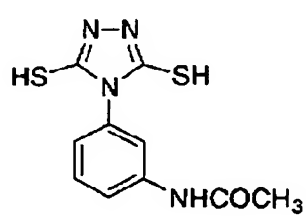

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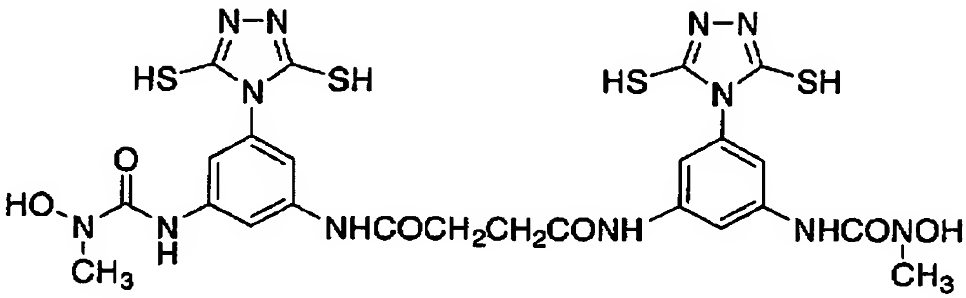

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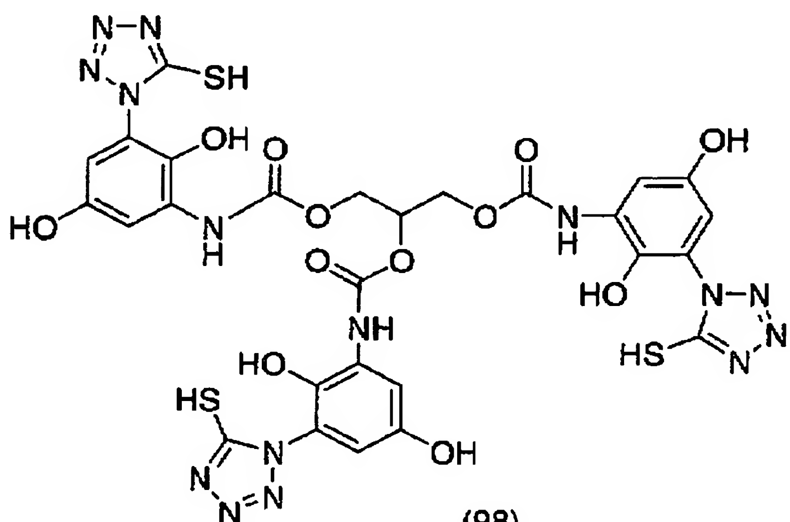


(98)

[0065]

These compounds can be easily synthesized by the known method.

The compound of formula (I) in the present invention can be used independently as only one compound, but it is preferred to use two compounds or more in combination. When two or more types of compounds are used in combination, those may be added to the same layer or the different layers, whereby addition methods may be different from each other.

[0066]

The compound represented by general formula (I) in the present invention preferably is added to a image forming layer and more preferably is to be added at an emulsion making process. In the case, wherein these compounds are added at an emulsion making process, these compounds may be added at any step in the process. For example, the silver halide grain forming step, a step before starting of salt washing-out step, the salt washing-out step, the step before chemical ripening, the chemical ripening step, the step before prepraring a final emulsion and the like are described. Also, the addition can be performed in the plural divided steps in the process. It is preferred to be added in an image forming layer, but also to be diffused at a coating step from a protective layer or an intermediate layer adjacent to the image forming layer, wherein these compounds are added in the protective layer or the intermediate layer in combination with their addition to the image forming layer.

The preferred addition amount is largely depend on the addition method or the type of compound described above, but generally 1×10^{-6} mol to 1 mol per one mol of photosensitive silver halide, preferably 1×10^{-5} mol to 5×10^{-1} mol, and more preferably 1×10^{-4} mol to 1×10^{-1} mol.

[0067]

The compound represented by general formula (I) in the present invention can be added by dissolving in water or water-soluble solvent such as methanol, ethanol and the like or a mixed solution thereof. At this time, pH may be arranged suitably by an acid or an alkaline and a surfactant can be coexisted. Further, these compounds may be added by dissolving in an organic solvent having

high boiling point as an emulsified dispersion and also may be added as a solid dispersion.

[0068]

2. Photosensitive silver halide

1) Halogen composition

It is preferred that the photosensitive silver halide in the present invention has a silver iodide content of at least 5 mol% or more. Other components are not particularly limited and can be selected from silver chloride and silver bromide and organic silver salts such as silver thiocyanate, silver phosphate and the like, and particularly, silver bromide and silver chloride are preferable. By using such a silver halide having a high silver iodide content, a preferable photothermographic material having excellent image stability after development treatment, particularly showing remarkably small increase in fogging in irradiation with light can be designed.

[0069]

Further, it is more preferable that the silver iodide content is 40 mol% or more, and it is extremely preferable from the standpoint of image stability against irradiation with light after treatment when the silver iodide content is 85 mol% or more, or 90 mol% or more.

[0070]

The distribution of the halogen composition in a grain may be uniform or the halogen composition may be changed stepwise, or it may be changed

continuously. Further, a silver halide grain having a core/shell structure can be preferably used. Preferred structure is a twofold to fivefold structure and, more preferably, core/shell grain having a twofold to fourfold structure can be used. A core-high-silver iodide-structure which has a high content of silver iodide in the core part, and a shell-high-silver iodide-structure which has a high content of silver iodide in the shell part can also be preferably used. Further, a technique of localizing silver bromide or silver iodide on the surface of a grain as form epitaxial parts can also be preferably used.

[0071]

2) Grain size

A high iodide silver halide with silver iodide used in the present invention, grain size is particularly important. When the size of silver halide is large, the applicaton amount of silver halide required for accompliching the necessary maximum density is increased. The present inventors found out that, if the application amount of the silver halide having a composition of high silver iodide content that is preferably used in the present invention is large, development is noticeably restricted to deteriorate the sensitization, and furthermore, density stability with time of development is deteriorated, which are not preferable. Therefore, the present inventors found out that, when the grain size exceedes a predermined size, a maximum density could not be obtained for a predetermined time. On the other hand, as far as the addition amount is limited, silver iodide can exhibit sufficient developability.

[0072]

When silver halide with high content of silver iodide is used, it is necessary that the size of a silver halide grain is sufficiently smaller as compared with conventional silver bromide and silver iodobromide having low iodine content for attaining sufficient maximum optical density. The average grain size of silver halide of high iodide content is preferably 5 nm to 70 nm, more preferably 5 nm to 55 nm. It is particularly preferably 10 nm to 45 nm. The grain size referred to herein is observed by an electron microscope, and means the average diameter of a converted circle having the same area as the projected area.

[0073]

3) Application amount

The application amount of silver halide grains in the invention is 0.5 mol% to 15 mol%, preferably 0.5 mol% to 12 mol%, and further preferably 0.5 mol% to 10 mol% per one mol of silver of a non-photosensitive organic silver salt described later. It is more preferably 1 mol% to 9 mol%, particularly preferably 1 mol% to 7 mol%.

[0074]

4) Grain formation method

A forming method of photosensitive silver halide has been well known in the industry to which the invention pertains and methods can be employed that are disclosed in, for example, Research Disclosure, No. 17029, June, 1978 and U.S. Patent No. 3700458 and to be concrete, a method is employed in which a silver supplying compound and a halogen supplying compound are added into a gelatin solution or another polymer solution to thereby prepare a photosensitive silver

halide, followed by mixing with an organic silver salt. Other preferable methods are also disclosed in paragraphs from 0217 to 0224 of JP-A No. 11-119374, JP-A No. 11-352627, and Japanese Patent Application No. 2000-42336.

[0075]

5) Grain form

While examples of forms of silver halide grains in the invention are cube grains, octahedron grains, dodecahedron grains, tetrahedron grains, flat plate grains, sphere grains, rod grains, potato grains and the like, particularly preferable in the invention are dodecahedron grains and tetrahedron grains. The term "dodecahedron grain" means a grain having planes of (001), {1(-1)0} and {101} and the term "tetrahedron grain" means a grain having planes of (001), {100} and {101}. The {100} expresses a family of crystallographic planes equivalent to a (100) plane.

[0076]

Silver iodide of the invention can assume any of a β phase or a γ phase contained. The term "β phase" described above means a high silver iodide structure having a wurtzite structure of a hexagonal system and the term "γ phase" means a high silver iodide structure having a zinc blend structure of a cubic crystal system.

An average content of γ phase in the present invention is determined by a method presented by C.R.Berry. In the method, an average content of γ phase is calculated from the peak ratio of the intensity owing to γ phase (111) to that owing to β phase (100), (101), 002) in powder X ray diffraction method. Detail

description, for example, is described in Physical Review, Volume 161, No.3, p. 848 to 851 (1967).

[0077]

According to the method of forming flat plate grains of silver iodide, preferably used are those described in JP-A Nos. 59-119350 and 59-119344. As for forming dodecahedron grains, tetrahedron grains and octahedron grains, the methods described in Japanese Patent Application Nos. 2002-081020, 2002-87955 and 2002-91756 can be used for reference.

[0078]

The silver halide having high silver iodide content of the invention can take a complicated form, and as the preferable form, there are listed, for example, connecting particles as shown in R. L. JENKINS et al., J. of Phot. Sci. Vol. 28 (1980), p164, Fig. 1. Flat plate particles as shown in Fig. 1 of the same literature can also be preferably used. Particles obtained by rounding corners of silver halide particles can also be preferably used. The surface index (Mirror index) of the outer surface of a photosensitive silver halide particle is not particularly restricted, and it is preferable that the ratio occupied by the [100] surface is rich, because of showing high spectral sensitization efficiency when a spectral sensitizer is adsorbed. The ratio is preferably 50% or more, more preferably 65% or more, further preferably 80% or more. The ratio of the [100] surface, Mirror index, can be determined by a method described in T. Tani; J. Imaging Sci., 29, 165 (1985) utilizing adsorption dependency of the [111] surface and [100] surface in adsorption of a sensitizing dye.

[0079]

6) Heavy metal

The photosensitive silver halide grain of the invention may contain other heavy metals together with iridium. Specifically, metals or complexes of metals belonging to groups 8 to 10 of the periodic table (showing groups 1 to 18) can be contained. The metal or the center metal of the metal complex from groups 8 to 10 of the periodic table is preferably rhodium, ruthenium, iron, cobalt, chromium, osmium or rhenium. The metal complex may be used alone, or two or more kinds of complexes comprising identical or different species of metals may be used together.

A preferred content is within a range from 1×10^{-9} mol to 1×10^{-3} mol per one mol of silver. The heavy metals, metal complexes and the addition method thereof are described in JP-A No. 7-225449, in paragraph Nos. 0018 to 0024 of JP-A No.11-65021 and in paragraph Nos. 0227 to 0240 of JP-A No. 11-119374.

[0080]

In the present invention, a silver halide grain preferably is doped using a hexacyano iridium complex or a hexacyano complex of other heavy metals. The hexacyano metal complex includes, for example, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Ru(CN)_6]^{4-}$, $[Os(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$, $[Rh(CN)_6]^{3-}$, $[Ir(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, and $[Re(CN)_6]^{3-}$. In the invention, hexacyano Fe complex is preferred.

[0081]

Since the hexacyano complex exists in ionic form in an aqueous solution,

paired cation is not important and alkali metal ion such as sodium ion, potassium ion, rubidium ion, cesium ion and lithium ion, ammonium ion, alkyl ammonium ion (for example, tetramethyl ammonium ion, tetraethyl ammonium ion, tetrapropyl ammonium ion, and tetra(n-butyl) ammonium ion), which are easily misible with water and suitable to precipitation operation of a silver halide emulsion are preferably used.

[0082]

The hexacyano metal complex can be added while being mixed with water, as well as a mixed solvent of water and an appropriate organic solvent miscible with water (for example, alcohols, ethers, glycols, ketones, esters and amides) or gelatin.

[0083]

The adding amount of the hexacyano metal complex is preferably about 1×10^{-5} mol to 1×10^{-2} mol, preferably, 1×10^{-4} mol to 1×10^{-3} mol per one mol of silver.

[0084]

In order to allow the hexacyano metal complex to be present on the outermost surface of a silver halide grain, the hexacyano metal complex is directly added in any stage of: after completion of addition of an aqueous solution of silver nitrate used for grain formation, before completion of emulsion forming step prior to a chemical sensitization step, of conducting chalcogen sensitization such as sulfur sensitization, selenium sensitization and tellurium sensitization or noble

metal sensitization such as gold sensitization, during washing step, during dispersion step and before chemical sensitization step. In order not to grow the fine silver halide grain, the hexacyano metal complex is rapidly added preferably after the grain is formed, and it is preferably added before completion of the emulsion forming step.

[0085]

Addition of the hexacyano complex may be started after addition of 96% by mass of an entire amount of silver nitrate to be added for grain formation, more preferably started after addition of 98% by mass and, particularly preferably, started after addition of 99% by mass.

When any of the hexacyano metal complex is added after addition of an aqueous silver nitrate just before completion of grain formation, it can be adsorbed to the outermost surface of the silver halide grain and most of them form an insoluble salt with silver ions on the surface of the grain. Since the hexacyano iron (II) silver salt is a less soluble salt than AgI, re-dissolution with fine grains can be prevented and fine silver halide grains with smaller grain size can be prepared.

[0086]

Metal atoms that can be contained in the silver halide grain used in the invention (for example, $[Fe(CN)_6]^{4-}$), desalting method of a silver halide emulsion and chemical sensitization method are described in paragraph Nos. 0046 to 0050 of JP-A No.11-84574, in paragraph Nos. 0025 to 0031 of JP-A No.11-65021, and paragraph Nos. 0242 to 0250 of JP-A No.11-119374.

[0087]

9) Gelatin

As the gelatin contained the photosensitive silver halide emulsion used in the invention, various kinds of gelatins can be used. It is necessary to maintain an excellent dispersion state of a photosensitive silver halide emulsion in an organic silver salt containing coating solution, and low molecular weight gelatin having a molecular weight of 10,000 to 1,000,000 is preferably used. And phthalated gelatin is also preferably used. These gelatins may be used at grain formation or at the time of dispersion after desalting treatment and it is preferably used during grain formation.

[0088]

8) Chemical sensitization

The photosensitive silver halide in this invention can be used without chemical sensitization, but is preferably chemically sensitized by at least one of chalcogen sensitization method, gold sensitization method and reduction sensitization method. The chalcogen sensitization method includes sulfur sensitization method, selenium sensitization method and tellurium sensitization method.

[0089]

In sulfur sensitization, unstable sulfur compounds can be used. Such unstable sulfur compounds are described in P. Grafkides, Chemie et Pysique Photographique (Paul Momtel, 1987, 5th ed.,) and Research Disclosure (vol. 307,

Item 307105), and the like.

[0090]

As typical examples of sulfur sensitizer, known sulfur compounds such as thiosulfates(e.g., hypo), thioureas (e.g., diphenylthiourea, triethylthiourea, N-ethyl-N'-(4-methyl-2-thiazolyl)thiourea and carboxymethyltrimethylthiourea), thioamides(e.g., thioacetamide), rhodanines(e.g., diethylrhodanine, 5-benzylydene-N-ethylrhodanine), phosphinesulfides(e.g., trimethylphosphinesulfide), thiohydantoins, 4-oxo-oxazolidin-2-thione derivatives, disulfides or polysulfides(e.g., dimorphorinedisulfide, cystine, hexathiocan-thione), polythionates, sulfur element and active gelatin can be used. Specifically, thiosulfates, thioureas and rhodanines are preferred.

[0091]

In selenium sensitization, unstable selenium compounds can be used. These unstable selenium compounds are described in JP-B Nos.43-13489 and 44-15748, JP-A Nos.4-25832, 4-109340, 4-271341, 5-40324, and 5-11385, Japanese Patent Application Nos. 4-202415, 4-330495, 4-333030, 5-4203, 5-4204, 5-106977, 5-236538, 5-241642 and 5-286916, and the like.

[0092]

As typical examples of selenium sensitizer, colloidal metal selenide, selenoureas(eg., N,N-dimethylselenourea, trifluoromethylcarbonyl-trimethylselenourea and acetyltrimethylselemourea), selenamides(eg., selenamide and N,N-diethylphenylselenamide), phosphineselenides(eg.,

triphenylphosphineselenide and pentafluorophenyl-triphenylphosphineselenide), selenophosphates(e.g., tri-p-tolylselenophosphate and tri-n-butylselenophosphate), selenoketones(e.g., selenobenzophenone), isoselenocyanates, selenocarbonic acids, selenoesters, diacylselenides can be used. Furthermore, non-unstable selenium compounds such as selenius acid, selenocyanic acid, selenazoles and selenides described in JP-B Nos. 46-4553 and 52-34492 can also be used. Specifically, phosphineselenides, selenoureas and salts of selenocyanic acids are preferred.

[0093]

In the tellurium sensitization, unstable tellurium compounds are used. Unstable tellurium compounds described in JP-A Nos.4-224595, 4-271341, 4-333043, 5-303157, 6-27573, 6-175258, 6-180478, 6-208186, 6-208184, 6-317867, 7-140579, 7-301879, 7-301880 and the like, can be used as tellurium sensitizer.

[0094]

As typical examples of tellurium sensitizer, phosphinetellurides(e.g., butyl-diisopropylphosphinetelluride, tributylphosphinetelluride, tributoxyphosphinetelluride and ethoxy-diphenylphosphinetellride), diacyl(di)tellurides(e.g.,bis(diphenylcarbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl)ditelluride, bis(N-phenyl-N-benzylcarbamoyl)telluride and bis(ethoxycarmonyl)telluride),telluroureas(e.g., N,N'-dimethylethylenetellurourea and N,N'-diphenylethylenetellurourea), telluramides, telluroesters are used. Specifically, diacyl(di)tellurides and phosphinetellurides are preferred. Especially, the compounds described in paragraph No. 0030 of JP-A No.11-65021

and compounds represented by the general formula (II), (III) and (IV) in JP-A No.5-313284 are more preferred.

[0095]

Selenium sensitization and tellurium sensitization are preferred as chalcogen sensitization and specifically, tellurium sensitization is more preferred.

[0096]

In gold sensitization, gold sensitizer described in P. Grafkides, Chemie et Pysique Photographique (Paul Momtel, 1987, 5th ed.,) and Research Disclosure (vol. 307, Item 307105) can be used. To speak concretely, chloroauric acid, potassium chloroaurate, potassium aurithiocyanate, gold sulfide, gold selenide and the like can be used. In addition to these, the gold compounds described in U.S.Patent Nos. 2642361, 5049484, 5049485, 5169751, and 5252455, Belg. Patent No. 691857, and the like can also be used. And another novel metal salts except gold such as platinum, palladium, iridium and so on described in P. Grafkides, Chemie et Pysique Photographique (Paul Momtel, 1987, 5th ed.,) and Research Disclosure (vol. 307, Item 307,105) can be used.

[0097]

The gold sensitization can be used independently, but it is preferably used in combination with the above chalcogen sensitization. Specifically, these sensitizations are gold-sulfur sensitization (gold-plus-sulfur sensitization), gold-selenium sensitization, gold-tellurium sensitization, gold-sulfur-selenium sensitization, gold-sulfur-tellurium sensitization, gold-selenium-tellurium

sensitization and gold-sulfur-selenium-tellurium sensitization.

[0098]

In the invention, chemical sensitization can be applied at any time so long as it is after grain formation and before coating, and it can be applied, after desalting, (1) before spectral sensitization, (2) simultaneously with spectral sensitization, (3) after spectral sensitization and (4) just before coating.

[0099]

The amount of chalcogen sensitizer used in the invention may vary depending on the silver halide grain used, the chemical ripening condition and the like and it is used by about 10^{-8} mol to 10^{-1} mol, preferably, 10^{-7} mol to 10^{-2} mol per one mol of the silver halide.

[0100]

Similarly, the addition amount of the gold sensitizer used in the invention may vary depending on various conditions and it is generally about 10^{-7} mol to 10^{-2} mol and, more preferably, 10^{-6} mol to 5×10^{-3} mol per one mol of the silver halide. There is no particular restriction on the condition for the chemical sensitization in the invention and, appropriately, pAg is 8 or less, preferably, 7.0 or less, more preferably, 6.5 or less and, particularly preferably, 6.0 or less, and pAg is 1.5 or more, preferably, 2.0 or more and, particularly preferably, 2.5 or more; pH is 3 to 10, preferably, 4 to 9; and temperature is at 20°C to 95°C, preferably, 25°C to 80°C.

[0101]

In the invention, reduction sensitization can also be used in combination with the chalcogen sensitization or the gold sensitization. It is specifically preferred to use in combination with the chalcogen sensitization.

As the specific compound for the reduction sensitization, ascorbic acid, thiourea dioxide or dimethylamine borane is preferred, as well as use of stannous chloride, aminoimino methane sulfonic acid, hydrazine derivatives, borane compounds, silane compounds and polyamine compounds are preferred. The reduction sensitizer may be added at any stage in the photosensitive emulsion production process from crystal growth to the preparation step just before coating. Further, it is preferred to apply reduction sensitization by ripening while keeping pH to 8 or higher and pAg to 4 or lower for the emulsion, and it is also preferred to apply reduction sensitization by introducing a single addition portion of silver ions during grain formation.

The addition amount of the reduction sensitizer may also vary depending on various conditions and it is generally about 10^{-7} mol to 10^{-1} mol and, more preferably, 10^{-6} mol to 5×10^{-2} mol per one mol of the silver halide.

[0102]

In the silver halide emulsion used in the invention, a thiosulfonic acid compound may be added by the method shown in EP-A No. 293917.

The photosensitive silver halide grain in the invention can be chemically unsensitized, but is preferably chemically sensitized by at least one method of gold sensitization method and chalcogen sensitization method for the purpose of designing a high-photosensitive photothermographic material.

[0103]

9) Compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons

The photothermographic material of the invention preferably contains a compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons. The said compound can be used in combination with various chemical sensitizers described above to increase the sensitivity of silver halide.

[0104]

As the compound that can be one-electron-oxidized to provide a one-electron oxidation product which releases one or more electrons is a compound selected from the following Types 1 to 5.

[0105]

(Type 1) a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases at least two electrons, due to being subjected to a subsequent bond cleavage reaction;

(Type 2) a compound that has at least two types adsorptive to the silver halide and can be one-electron-oxidized to provide a one-electron oxidation product which further releases one electron, due to being subjected to a subsequent bond cleavage reaction;

(Type 3) a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which further releases at least one electron after being subjected to a subsequent bond formation;

(Type 4) a compound that can be one-electron-oxidized to provide a one-electron oxidation product which further releases at least one electron after a subsequent intramolecular ring cleavage reaction; and

(Type 5) a compound represented by X-Y, in which X represents a reducible type and Y represents a leaving type, and convertable by one-electron-oxidizing the reducible type to a one-electron oxidation product which can be converted into an X radical by eliminating the leaving type in a subsequent X-Y bond cleavage reaction, one electron being released from the X radical.

[0106]

Each compound of Type 1 and Types 3 to 5 preferably is a "compound having a sensitizing dye moiety" or a "compound having an adsorptive type to the silver halide". More preferred is a "compound having an adsorptive type to the silver halide". Each compound of Types 1 to 4 more preferably is a "compound having a heterocyclic type containing nitrogen atoms substituted by two or more mercapto types".

[0107]

The compound of Types 1 to 5 will be described in detail below.

In the compound of Type 1, the term "the bond cleavage reaction" specifically means a cleavage reaction of a bond of carbon-carbon, carbon-silicon, carbon-hydrogen, carbon-boron, carbon-tin or carbon-germanium. Cleavage of a carbon-hydrogen bond may be followed after the cleavage reaction. The compound of Type 1 can be one-electron-oxidized to be converted into the one-electron oxidation product, and thereafter can release further two or more electrons,

preferably three or more electrons with the bond cleavage reaction.

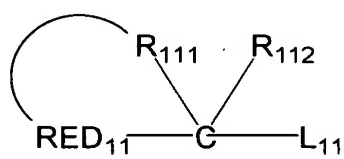
[0108]

The compound of Type 1 is preferably represented by any one of general formulae (A), (B), (1), (2) and (3).

[0109]

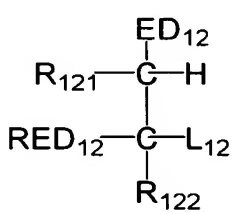
[F11]

General formula(A)



[0110] [F12]

General formula(B)



[0111]

In general formula (A), RED_{11} represents a reducible group that can be one-electron-oxidized, and L_{11} represents a leaving group. R_{112} represents a hydrogen atom or a substituent. R_{111} represents a nonmetallic atomic group forming a tetrahydro-, hexahydro- or octahydro-derivative of a 5- or 6-membered aromatic ring including aromatic heterocycles.

[0112]

In general formula (B), RED_{12} represents a reducible group that can be one-electron-oxidized, and L_{12} represents a leaving group. R_{121} and R_{122} each represent a hydrogen atom or a substituent. ED_{12} represents an electron-donating group. In general formula (B), R_{121} and RED_{12}, R_{121} and R_{122}, and ED_{12} and RED_{12} may bond together to form a ring structure, respectively.

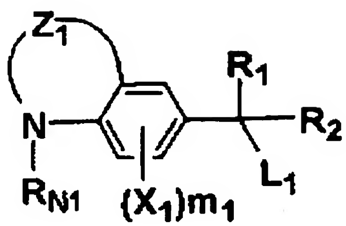
[0113]

In the compound represented by general formula (A) or (B), the reducible group of RED_{11} or RED_{12} is one-electron-oxidized, and thereafter the leaving group of L_{11} or L_{12} is spontaneously eliminated in the bond cleavage reaction. Further two or more, preferably three or more electrons can be released with the bond cleavage reaction.

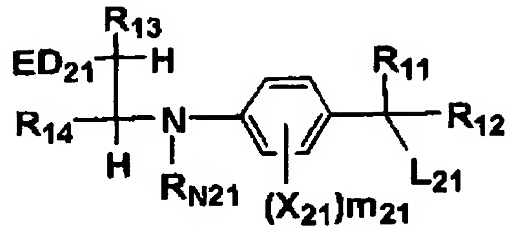
[0114]

[F13]

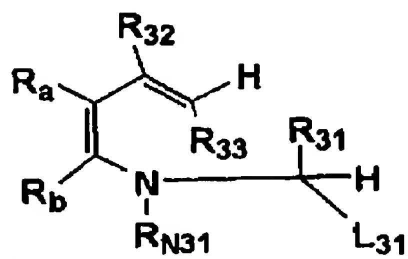
General formula (1)



General formula (2)



General formula (3)



[0115]

In general formula (1), Z_1 represents an atomic group forming a 6-membered ring with a nitrogen atom and 2 carbon atoms in a benzene ring; R_1, R_2 and R_{N1} each represent a hydrogen atom or a substituent; X_1 represents a substituent capable of substituting for a hydrogen atom on a benzene ring; m_1 represents an integer from 0 to 3; and L_1 represents a leaving group. In general formula (2), ED_{21} represents an electron-donating group; R_{11}, R_{12}, R_{N21}, R_{13} and R_{14} each represent a hydrogen atom or a substituent; X_{21} represents a substituent capable of substituting for a hydrogen atom on a benzene ring; m_{21} represents an integer from 0 to 3; and L_{21} represents a leaving group. R_{N21}, R_{13}, R_{14}, X_{21} and ED_{21} may bond to each other to form a ring structure. In general formula (3), R_{32}, R_{33}, R_{31}, R_{N31}, R_a and R_b each represent a hydrogen atom or a substituent; and L_{31} represents a leaving group. Incidentally, R_a and R_b bond together to form an

aromatic ring when R_{N31} is not an aryl group.

[0116]

After the compound is one-electron-oxidized, the leaving group of L_1, L_{21} or L_{31} is spontaneously eliminated in the bond cleavage reaction. Further two or more, preferably three or more electrons can be released with the bond cleavage reaction.

[0117]

First, the compound represented by general formula (A) will be described in detail below.

In general formula (A), the reducible group of RED_{11} can be one-electron-oxidized and can bond to after-mentioned R_{111} to form the particular ring structure. Specifically, the reducible group may be a divalent group provided by removing one hydrogen atom from the following monovalent group at a position suitable for ring formation.

The monovalent group may be an alkylamino group; an arylamino group such as an anilino group and a naphthylamino group; a heterocyclic amino group such as a benzthiazolylamino group and a pyrrolylamino group; an alkylthio group; an arylthio group such as a phenylthio group; a heterocyclic thio group; an alkoxy group; an aryloxy group such as a phenoxy group; a heterocyclic oxy group; an aryl group such as a phenyl group, a naphthyl group and an anthranil group; or an aromatic or nonaromatic heterocyclic group, containing at least one heteroatom selected from the group consisting of a nitrogen atom, a sulfur atom, an oxygen atom and a selenium atom, which has a 5- to 7-membered, monocyclic or

condensed ring structure such as a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinoxaline ring, a tetrahydroquinazoline ring, an indoline ring, an indole ring, an indazole ring, a carbazole ring, a phenoxazine ring, a phenothiazine ring, a benzothiazoline ring, a pyrrole ring, an imidazole ring, a thiazoline ring, a piperidine ring, a pyrrolidine ring, a morpholine ring, a benzimidazole ring, a benzimidazoline ring, a benzoxazoline ring and a methylenedioxyphenyl ring. RED_{11} is hereinafter described as the monovalent group for convenience. The monovalent groups may have a substituent.

[0118]

Examples of the substituent include halogen atoms; alkyl groups including aralkyl groups, cycloalkyl groups, active methine groups, etc.; alkenyl groups; alkynyl groups; aryl groups; heterocyclic groups, which may bond at any position; heterocyclic groups containing a quaternary nitrogen atom such as a pyridinio group, an imidazolio group, a quinolinio group and an isoquinolinio group; acyl groups; alkoxycarbonyl groups; aryloxycarbonyl groups; carbamoyl groups; a carboxy group and salts thereof; sulfonylcarbamoyl groups; acylcarbamoyl groups; sulfamoylcarbamoyl groups; carbazoyl groups; oxalyl groups; oxamoyl groups; a cyano group; carbonimidoyl groups; thiocarbamoyl groups; a hydroxy group; alkoxy groups, which may contain a plurality of ethyleneoxy groups or propyleneoxy groups as a repetition unit; aryloxy groups; heterocyclic oxy groups; acyloxy groups; alkoxy or aryloxy carbonyloxy groups; carbamoyloxy groups; sulfonyloxy groups; amino groups; alkyl, aryl or heterocyclic amino groups; acylamino groups; sulfoneamide groups; ureide groups; thioureide groups; imide groups; alkoxy or aryloxy carbonylamino groups; sulfamoylamino groups;

semicarbazide groups; thiosemicarbazide groups; hydrazino groups; ammonio groups; oxamoylamino groups; alkyl or aryl sulfonylureide groups; acylureide groups; acylsulfamoylamino groups; a nitro group; a mercapto group; alkyl, aryl or heterocyclic thio groups; alkyl or aryl sulfonyl groups; alkyl or aryl sulfinyl groups; a sulfo group and salts thereof; sulfamoyl groups; acylsulfamoyl groups; sulfonylsulfamoyl groups and salts thereof; groups containing a phosphoric amide or phosphate ester structure; etc. These substituents may be further substituted by these substituents.

[0119]

RED_{11} is preferably an alkylamino group, an arylamino group, a heterocyclic amino group, an aryl group, an aromatic heterocyclic group, or nonaromatic heterocyclic group. RED_{11} is more preferably an arylamino group (particularly an anilino group), or an aryl group (particularly a phenyl group). When RED_{11} has a substituent, preferred as a substituent include halogen atoms, alkyl groups, alkoxy groups, carbamoyl groups, sulfamoyl groups, acylamino groups, sulfoneamide groups. When RED_{11} is an aryl group, it is preferred that the aryl group has at least one "electron-donating group". The "electron-donating group" is a hydroxy group; an alkoxy group; a mercapto group; a sulfoneamide group; an acylamino group; an alkylamino group; an arylamino group; a heterocyclic amino group; an active methine group; an electron-excess, aromatic, heterocyclic group with a 5- membered monocyclic ring or a condensed-ring including at least one nitrogen atom in the ring such as an indolyl group, a pyrrolyl group, an imidazolyl group, a benzimidazolyl group, a thiazolyl group, a benzthiazolyl group and an indazolyl group; a nitrogen-containing, nonaromatic

heterocyclic group that substitutes at the nitrogen atom, such as so-called cyclic amino group like pyrrolidinyl group, an indolinyl group, a piperidinyl group, a piperazinyl group and a morpholino group; etc. The active methine group is a methine group having two "electron-withdrawing groups", and the "electron-withdrawing group" is an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfamoyl group, a trifluoromethyl group, a cyano group, a nitro group or a carbonimidoyl group. The two electron-withdrawing groups may bond together to form a ring structure.

[0120]

In general formula (A), specific examples of L_{11} include a carboxy group and salts thereof, silyl groups, a hydrogen atom, triarylboron anions, trialkylstannyl groups, trialkylgermyl groups and a $-CR_{C1}R_{C2}R_{C3}$ group. When L_{11} represents a silyl group, the silyl group is specifically a trialkylsilyl group, an aryldialkylsilyl group, a triarylsilyl group, etc, and they may have a substituent.

[0121]

When L_{11} represents a salt of a carboxy group, specific examples of a counter ion to form the salt include alkaline metal ions, alkaline earth metal ions, heavy metal ions, ammonium ions, phosphonium ions, etc. Preferred as a counter ion are alkaline metal ions and ammonium ions, most preferred are alkaline metal ions such as Li^+, Na^+ and K^+.

[0122]

When L_{11} represents a $-CR_{C1}R_{C2}R_{C3}$ group, R_{C1}, R_{C2} and R_{C3} independently represent a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkylthio group, an arylthio group, an alkylamino group, an arylamino group, a heterocyclic amino group, an alkoxy group, an aryloxy group or a hydroxy group. R_{C1}, R_{C2} and R_{C3} may bond to each other to form a ring structure, and may have a substituent. Incidentally, when one of R_{C1}, R_{C2} and R_{C3} is a hydrogen atom or an alkyl group, there is no case where the other two of them are a hydrogen atom or an alkyl group. R_{C1}, R_{C2} and R_{C3} are preferably an alkyl group, an aryl group (particularly a phenyl group), an alkylthio group, an arylthio group, an alkylamino group, an arylamino group, a heterocyclic group, an alkoxy group or a hydroxy group, respectively. Specific examples thereof include a phenyl group, a *p*-dimethylaminophenyl group, a *p*-methoxyphenyl group, a 2,4-dimethoxyphenyl group, a *p*-hydroxyphenyl group, a methylthio group, a phenylthio group, a phenoxy group, a methoxy group, an ethoxy group, a dimethylamino group, an *N*-methylanilino group, a diphenylamino group, a morpholino group, a thiomorpholino group, a hydroxy group, etc. Examples of the ring structure formed by R_{C1}, R_{C2} and R_{C3} include a 1,3-dithiolane-2-yl group, a 1,3-dithiane-2-yl group, an *N*-methyl-1,3-thiazolidine-2-yl group, an *N*-benzyl-benzothiazolidine-2-yl group, etc.

[0123]

It is also preferred that the $-CR_{C1}R_{C2}R_{C3}$ group is the same as a residue provided by removing L_{11} from general formula (A) as a result of selecting each of R_{C1}, R_{C2} and R_{C3} as above.

[0124]

In general formula (A), L_{11} is preferably a carboxy group or a salt thereof, or a hydrogen atom, more preferably a carboxy group or a salt thereof.

[0125]

When L_{11} represents a hydrogen atom, the compound represented by general formula (A) preferably has a base moiety. After the compound represented by general formula (A) is oxidized, the base moiety acts to eliminate the hydrogen atom of L_{11} and to release an electron.

[0126]

The base is specifically a conjugate base of an acid with a pKa value of approximately 1 to 10. For example, the base moiety may contain a structure of a nitrogen-containing heterocycle such as pyridine, imidazole, benzoimidazole and thiazole; aniline; trialkylamine; an amino group; a carbon acid such as an active methylene anion; a thioacetic acid anion; carboxylate ($-COO^-$); sulfate ($-SO_3^-$); amineoxide ($>N^+(O^-)-$); and derivatives thereof. The base is preferably a conjugate base of an acid with a pKa value of approximately 1 to 8, more preferably carboxylate, sulfate or amineoxide, particularly preferably carboxylate. When these bases have an anion, the compound of general formula (A) may have a counter cation. Examples of the counter cation include alkaline metal ions, alkaline earth metal ions, heavy metal ions, ammonium ions, phosphonium ions, etc. The base moiety may be at an optional position of the compound represented by general formula (A). The base moiety may be connected to RED_{11}, R_{111} or R_{112} in general formula (A), and to a substituent thereon.

[0127]

In general formula (A), R_{112} represents a substituent capable of substituting a hydrogen atom or a carbon atom therewith, provided that R_{112} and L_{11} do not represent the same group.

R_{112} preferably represents a hydrogen atom, an alkyl group, an aryl group (such as a phenyl group), an alkoxy group (such as a methoxy group, a ethoxy group, a benzyloxy group), a hydroxy group, an alkylthio group, (such as a methylthio group, a butylthio group), and amino group, an alkylamino group, an arylamino group, a heterocyclic amino group or the like; and more preferably represents a hydrogen atom, an alkyl group, an alkoxy group, a hydroxy group, a phenyl group and an alkylamino group.

[0128]

Ring structures formed by R_{111} in general formula (A) are ring structures corresponding to a tetrahydro structure, a hexahydro structure, or an octahydro structure of a five-membered or six-membered aromatic ring (including an aromatic hetro ring), wherein a hydro structure means a ring structure in which partial hydrogenation is performed on a carbon-carbon double bond (or a carbon-nitrogen double bond) contained in an aromatic ring (an aromatic hetero ring) as a part thereof, wherein the tetrahydro structure is a structure in which 2 carbon-carbon double bonds (or carbon-nitrogen double bonds) are hydrogenated, the hexahydro structure is a structure in which 3 carbon-carbon double bonds (or carbon-nitrogen double bonds) are hydrogenated, and the octahydro structure is a structure in which 4 carbon-carbon double bonds (or carbon-nitrogen double

bonds) are hydrogenated. Hydrogenation of an aromatic ring produces a partially hydrogenated non-aromatic ring structure.

[0129]

Examples include a pyrrolidine ring, an imidazolidine ring, a thiazolidine ring, a pyrazolidine ring, an oxazolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydropyrimidine ring, a piperazine ring, a tetralin ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring and a tetrahydroquinoxaline ring, a tetrahydrocarbazole ring, an octahydrophenanthridine ring and the like. The ring structures may have any substituent therein.

[0130]

More preferable examples of a ring structure forming R_{111} include a pyrrolidine ring, an imidazolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydropyrimidine ring, a piperazine ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring, a tetrahydroquinoxaline ring and a tetracarbazole ring. Particularly preferable examples include a pyrrolidine ring, a piperidine ring, a piperazine ring, a tetrahydropyridine ring, a tetrahydroquinoline ring, a tetrahydroisoquinoline ring, a tetrahydroquinazoline ring and a tetrahydroquinoxaline ring; and most preferable examples include a pyrrolidine ring, a piperidine ring, a tetrahydropyridine ring, a tetrahydroquinoline ring and a tetrahydroisoquinoline ring.

[0131]

In general formula (B), RED_{12} and L_{12} represent groups having the respective same meanings as RED_{11} and L_{11} in general formula (A), and have the respective same preferable ranges as RED_{11} and L_{11} in general formula (A). RED_{12} is a monovalent group except a case where RED_{12} forms the following ring structure and to be concrete, there are exemplified groups each with a name of a monovalent group described as RED_{11}. RED_{121} and L_{122} represent groups having the same meaning as R_{112} in general formula (A), and have the same preferable range as R_{112} in general formula (A). ED_{12} represents an electron-donating group. Each pair of R_{121} and RED_{12}; R_{121} and R_{122}; or ED_{12} and RED_{12} may form a ring structure by bonding with each other.

[0132]

An electron-donating group represented by RED_{12} in general formula (B) is the same as an electron-donating group described as a substituent when RED_{11} represents an aryl group. Preferable examples of RED_{12} include a hydroxy group, an alkoxy group, a mercapto group, a sulfonamide group, an alkylamino group, an arylamino group, an active methine group, an electron-excessive aromatic heterocyclic group in a five-membered single ring or fused ring structure containing at least one nitrogen atom in a ring structure as part of the ring, a non-aromatic nitrogen containing hetrocyclic group having a nitrogen atom as a substitute, and a phenyl group substituted with an electron donating group described above, and more preferable examples thereof include a non-aromatic nitrogen containing heterocyclic group further substituted with a hydroxy group, a mercapto group, a sulfonamide group, an alkylamino group, an arylamino group, an active methine group, or a nitrogen atom; and a phenyl group substituted with

an electron-donating group described above (for example, a p-hydroxyphenyl group, a p-dialkylaminophenyl group, an o- or p-dialkoxyphenyl group and the like).

[0133]

In general formula (B), R_{121} and RED_{12}; R_{122} and R_{121}; or ED_{12} and RED_{12} may bond to each other to form a ring structure. A ring structure formed here is a non-aromatic carbon ring or hetero ring in a 5- to 7-membered single ring or fused ring structure which is substituted or unsubstituted. Concrete examples of a ring structure formed from R_{121} and RED_{12} include, in addition to the examples of the ring structure formed by R_{111} in general formula (A), a pyrroline ring, an imidazoline ring, a thiazoline ring, a pyrazoline ring, an oxazoline ring, an indan ring, a morphorine ring, an indoline ring, a tetrahydro-1,4-oxazine ring, 2,3-dihydrobenzo-1,4-oxazine ring, a tetrahydro-1,4-thiazine ring, 2,3-dihydrobenzo-1,4-thiazine ring, 2,3-dihydrobenzofuran ring, 2,3-dihydrobenzothiophene ring and the like. In formation of a ring structure from ED_{12} and RED_{12}, ED_{12} is preferably an amino group, an alkylamino group or an arylamino group and concrete examples of the ring structure include a tetrahyropyrazine ring, a piperazine ring, a tetrahydroquinoxaline ring, a tetrahydroisoquinoline ring and the like. Concrete examples of a ring structure formed from R_{122} and R_{121} include a cyclohexane ring, a cyclopentane ring and the like.

[0134]

Below, description will be given of general formulae (1) to (3).

In general formulae (1) to (3), R_1, R_2, R_{11}, R_{12} and R_{31} represent the same

meaning as R_{112} of general formula (A) and have the same preferable range as R_{112} of general formula (A). L_1, L_{21} and L_{31} independently represents the same leaving groups as the groups shown as concrete examples in description of L_{11} of general formula (A) and also have the same preferable range as L_{11} of general formula (A). The substituents represented by X_1 and X_{21} are the same as the examples of substituents of RED_{11} of general formula (A) and have the same preferable range as RED_{11} of general formula (A). m_1 and m_2 are preferably integers from 0 to 2 and more preferably integer of 0 or 1.

[0135]

When R_{N1}, R_{N21} and R_{N31} each represent a substituent, preferred as a substituent include an alkyl group, an aryl group or a heterocyclic group, and may further have a substituent. Each of R_{N1}, R_{N21} and R_{N31} is preferably a hydrogen atom, an alkyl group or an aryl group, more preferably a hydrogen atom or an alkyl group.

[0136]

When R_{13}, R_{14}, R_{32}, R_{33}, R_a and R_b independently represent a substituent, the substituent is preferably an alkyl group, an aryl group, an acyl group, an alkoxycarbonyl group, a carbamoyl group, a cyano group, an alkoxy group, an acylamino group, a sulfoneamide group, a ureide group, a thiouredide group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group, or a sulfamoyl group.

[0137]

The 6-membered ring formed by Z_1 in general formula (1) is a nonaromatic heterocycle condensed with the benzene ring in general formula (1). The ring structure containing the nonaromatic heterocycle and the benzene ring to be condensed may be specifically a tetrahydroquinoline ring, a tetrahydroquinoxaline ring, or a tetrahydroquinazoline ring, which may have a substituent.

[0138]

In general formula (2), ED_{21} is the same as ED_{12} in general formula (B) with respect to the meanings and preferred embodiments.

[0139]

In general formula (2), any two of R_{N21}, R_{13}, R_{14}, X_{21} and ED_{21} may bond together to form a ring structure. The ring structure formed by R_{N21} and X_{21} is preferably a 5- to 7-membered, carbocyclic or heterocyclic, nonaromatic ring structure condensed with a benzene ring, and specific examples thereof include a tetrahydroquinoline ring, a tetrahydroquinoxaline ring, an indoline ring, a 2,3-dihydro-5,6-benzo-1,4-thiazine ring, etc. Preferred are a tetrahydroquinoline ring, a tetrahydroquinoxaline ring and an indoline ring.

[0140]

When R_{N31} is a group other than an aryl group in general formula (3), R_a and R_b bond together to form an aromatic ring. The aromatic ring is an aryl group such as a phenyl group and a naphthyl group, or an aromatic heterocyclic group such as a pyridine ring group, a pyrrole ring group, a quinoline ring group and an indole ring group, preferably an aryl group. The aromatic ring group may have a

substituent.

In general formula (3), R_a and R_b preferably bond together to form an aromatic ring, particularly a phenyl group.

[0141]

In general formula (3), R_{32} is preferably a hydrogen atom, an alkyl group, an aryl group, a hydroxy group, an alkoxy group, a mercapto group or an amino group. When R_{32} is a hydroxy group, R_{33} is preferably an electron-withdrawing group. The electron-withdrawing group is the same as described above, preferably an acyl group, an alkoxycarbonyl group, a carbamoyl group or a cyano group.

[0142]

The compound of Type 2 will be described below.

According to the compound of Type 2, the "bond cleavage reaction" is a cleavage reaction of a bond of carbon-carbon, carbon-silicon, carbon-hydrogen, carbon-boron, carbon-tin or carbon-germanium. Cleavage of a carbon-hydrogen bond may be caused with the cleavage reaction.

[0143]

The compound of Type 2 has two or more, preferably 2 to 6, more preferably 2 to 4, adsorbent groups to the silver halide. The adsorptive group is further preferably a mercapto-substituted, nitrogen-containing, heterocyclic group. The adsorptive group will hereinafter be described.

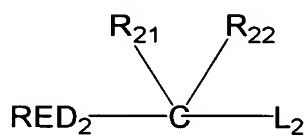
[0144]

The compound of Type 2 is preferably represented by the following general formula (C).

[0145]

[F14]

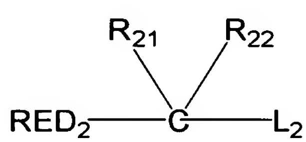
General formula (C)



[0146]

In the compound represented by general formula (C), the reducible group of RED_2 is one-electron-oxidized, and thereafter the leaving group of L_2 is spontaneously eliminated, thus a C (carbon atom)-L_2 bond is cleaved, in the bond cleavage reaction. Further one electron can be released with the bond cleavage reaction.

General formula (C)

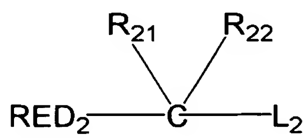


[0147]

In general formula (C), RED_2 is the same as RED_{12} in general formula (B) with respect to the meanings and preferred embodiments. L_2 is the same as L_{11} in general formula (A) with respect to the meanings and preferred embodiments. Incidentally, when L_2 is a silyl group, the compound of general formula (C) has

two or more mercapto-substituted, nitrogen-containing, heterocyclic groups as the adsorbent groups. R_{21} and R_{22} each represent a hydrogen atom or a substituent, and are the same as R_{112} in general formula (A) with respect to the meanings and preferred embodiments. RED_2 and R_{21} may bond together to form a ring structure.

General formula (C)

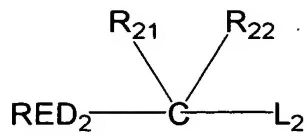


[0148]

The ring structure is a 5- to 7-membered, monocyclic or condensed, carbocyclic or heterocyclic, nonaromatic ring, and may have a substituent. Incidentally, there is no case where the ring structure corresponds to a tetrahydro-, hexahydro- or octahydro-derivative of an aromatic ring or an aromatic heterocycle. The ring structure is preferably such that corresponds to a dihydro-derivative of an aromatic ring or an aromatic heterocycle, and specific examples thereof include a 2-pyrroline ring, a 2-imidazoline ring, a 2-thiazoline ring, a 1,2-dihydropyridine ring, a 1,4-dihydropyridine ring, an indoline ring, a benzoimidazoline ring, a benzothiazoline ring, a benzoxazoline ring, a 2,3-dihydrobenzothiophene ring, a 2,3-dihydrobenzofuran ring, a benzo-α-pyran ring, a 1,2-dihydroquinoline ring, a 1,2-dihydroquinazoline ring, a 1,2-dihydroquinoxaline ring, etc. Preferred are a 2-imidazoline ring, a 2-thiazoline ring, an indoline ring, a benzoimidazoline ring, a benzothiazoline ring, a benzoxazoline ring, a 1,2-dihydro pyridine ring, a 1,2-dihydroquinoline ring, a 1,2-dihydroquinazoline ring and a 1,2-dihydroquinoxaline ring, more preferred are an indoline ring, a benzoimidazoline ring, a benzothiazoline ring and a 1,2-dihydroquinoline ring, particularly preferred is an

indoline ring.

General formula (C)



[0149]

The compound of Type 3 will be described below.

According to the compound of Type 3, "bond formation" means that a bond of carbon-carbon, carbon-nitrogen, carbon-sulfur, carbon-oxygen, etc. is formed.

[0150]

The compound of Type 3 is preferably a compound that the one-electron oxidation product which is produced by one electron oxidation reacts with a site of reactive groups (a carbon-carbon double bond, a carbon-carbon triple bond, an aromatic group and a benzo-condensed, nonaromatic heterocyclic group) that coexists in the same molecule to form a bond, and thereafter further can release one or more elecrons.

[0151]

To be more detailed, a one-electron oxidized product (a cation radical species or a neutral radical species generated by elimination of a proton therefrom) formed by one electron oxidizing a compound of Type 3 reacts with a reactive group described above coexisting in the same molecule to form a bond and form a radical species having a new ring structure therein. The radical species have a feature to release a second electron directly or in company with elimination of a

proton therefrom.

[0152]

One of compounds of Type 3 has a chance to further release one or more electrons, in a ordinary case two or more electrons, after formation of a two-electron oxidized product, after receiving a hydrolysis reaction in one case or after causing a tautomerization reaction accompanying direct migration of a proton in another case.

Alternatively, compounds of Type 3 also include a compound having an ability to further release one or more electron, in an ordinary case two or more electrons directly from a two-electron oxidized product, not by way of a tautomerization reaction.

[0153]

The compound of Type 3 is preferably represented by the following general formula (D).

[0154]

[F15]

General formula (D)

$$RED_3—L_3—Y_3$$

[0155]

In general formula (D), RED_3 represents a reducible group that can be one-electron-oxidized, and Y_3 represents a reactive group that reacts with the one-

electron-oxidized RED_3, specifically an organic group containing a carbon-carbon double bond, a carbon-carbon triple bond, an aromatic group or a benzo-condensed, nonaromatic heterocyclic group. L_3 represents a linking group that connects RED_3 and Y_3.

General formula (D)

$$RED_3 — L_3 — Y_3$$

[0156]

In general formula (D), RED_3 has the same meanings as RED_{12} in general formula (B). In general formula (D), RED_3 is preferably an arylamino group, a heterocyclic amino group, an aryloxy group, an arylthio group, an aryl group, or an aromatic or nonaromatic heterocyclic group that is preferably a nitrogen-containing heterocyclic group. RED_3 is more preferably an arylamino group, a heterocyclic amino group, an aryl group, or an aromatic or nonaromatic heterocyclic group. Preferred as the heterocyclic group are a tetrahydroquinoline ring group, a tetrahydroquinoxaline ring group, a tetrahydroquinazoline ring group, an indoline ring group, an indole ring group, a carbazole ring group, a phenoxazine ring group, a phenothiazine ring group, a benzothiazoline ring group, a pyrrole ring group, an imidazole ring group, a thiazole ring group, a benzoimidazole ring group, a benzoimidazoline ring group, a benzothiazoline ring group, a 3,4-methylenedioxyphenyl-1-yl group, etc.

Particularly preferred as RED_3 are an arylamino group (particularly an anilino group), an aryl group (particularly a phenyl group), and an aromatic or nonaromatic heterocyclic group.

[0157]

The aryl group represented by RED_3 preferably has at least one electron-donating group. The term "electron-donating group" means the same as above-mentioned electron-donating group.

[0158]

When RED_3 is an aryl group, more preferred as a substituent on the aryl group are an alkylamino group, a hydroxy group, an alkoxy group, a mercapto group, a sulfoneamide group, an active methine group, and a nitrogen-containing, nonaromatic heterocyclic group that substitutes at the nitrogen atom, furthermore preferred are an alkylamino group, a hydroxy group, an active methine group, and a nitrogen-containing, nonaromatic heterocyclic group that substitutes at the nitrogen atom, and the most preferred are an alkylamino group, and a nitrogen-containing, nonaromatic heterocyclic group that substitutes at the nitrogen atom.

[0159]

When Y_3 is an organic group containing carbon-carbon double bond (for example a vinyl group) having a substituent, more preferred as the substituent are an alkyl group, a phenyl group, an acyl group, a cyano group, an alkoxycarbonyl group, a carbamoyl group and an electron-donating group. The electron-donating group is preferably an alkoxy group; a hydroxy group (that may be protected by a silyl group, and examples of the silyl-protected group include a trimethylsilyloxy group, a *t*-butyldimethylsilyloxy group, a triphenylsilyloxy group, a triethylsilyloxy group, a phenyldimethylsilyloxy group, etc); an amino group; an alkylamino group; an arylamino group; a sulfoneamide group; an active methine

group; a mercapto group; an alkylthio group; or a phenyl group having the electron-donating group as a substituent.

[0160]

Incidentally, when the organic group containing the carbon-carbon double bond has a hydroxy group as a substituent, Y_3 contains a moiety of $>C_1=C_2(-OH)-$, which may be tautomerized into a moiety of $>C_1H-C_2(=O)-$. In this case, it is preferred that a substituent on the C_1 carbon is an electron-withdrawing group, and as a result, Y_3 has a moiety of an active methylene group or an active methine group. The electron-withdrawing group, which can provide such a moiety of an "active methylene group" or an "active methine group", may be the same as above-mentioned electron-withdrawing group on the methine group of the "active methine group".

[0161]

When Y_3 is an organic group containing a carbon-carbon triple bond (for example a ethynyl group) having a substituent, preferred as the substituent is an alkyl group, a phenyl group, an alkoxycarbonyl group, a carbamoyl group, an electron-donating group, etc.

[0162]

When Y_3 is an organic group containing an aromatic group, preferred as the aromatic group is an aryl group, particularly a phenyl group, having an electron-donating group as a substituent, and an indole ring group. The electron-donating group is preferably a hydroxy group, which may be protected by a silyl

group; an alkoxy group; an amino group; an alkylamino group; an active methine group; a sulfoneamide group; or a mercapto group.

[0163]

When Y_3 is an organic group containing a benzo-condensed, nonaromatic heterocyclic group, preferred as the benzo-condensed, nonaromatic heterocyclic group are groups having an aniline moiety, such as an indoline ring group, a 1,2,3,4-tetrahydroquinoline ring group, a 1,2,3,4-tetrahydroquinoxaline ring group and a 4-quinolone ring group.

[0164]

The reactive group of Y_3 is more preferably an organic group containing a carbon-carbon double bond, an aromatic group, or a benzo-condensed, nonaromatic heterocyclic group. Furthermore preferred are an organic group containing a carbon-carbon double bond; a phenyl group having an electron-donating group as a substituent; an indole ring group; and a benzo-condensed, nonaromatic heterocyclic group having an aniline moiety. The carbon-carbon double bond more preferably has at least one electron-donating group as a substituent.

[0165]

A case when the reactive group represented by Y_3 has the same partial structure as the reducible group represented by RED_3 as a result of selecting the reactive group as above is also a preferable example of a compound represented by General Formula (D).

[0166]

L_3 represents a linking group that connects RED_3 and Y_3, specifically a single bond, an alkylene group, an arylene group, a heterocyclic group, -O-, -S-, -NR_N-, -C(=O)-, -SO_2-, -SO-, -P(=O)-, or a combination thereof. R_N represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group. The linking group represented by L_3 may have a substituent. The linking group represented by L_3 may bond to each of RED_3 and Y_3 at an optional position such that the linking group substitutes optional one hydrogen atom of each RED_3 and Y_3.

[0167]

Preferred examples of L_3 include a single bond; alkylene groups, particularly a methylene group, an ethylene group or a propylene group; arylene groups, particularly a phenylene group; a -C(=O)- group; a -O- group; a -NH- group; -N(alkyl)- groups; and divalent linking groups of combinations thereof.

[0168]

When a cation radical ($X^{+}\cdot$) provided by oxidizing RED_3 or a radical ($X\cdot$) provided by eliminating a proton therefrom reacts with the reactive group represented by Y_3 to form a bond, it is preferable that they form a 3 to 7-membered ring structure containing the linking group represented by L_3. Thus, the radical ($X^{+}\cdot$or $X\cdot$) and the reactive group of Y are preferably connected though 3 to 7 atoms.

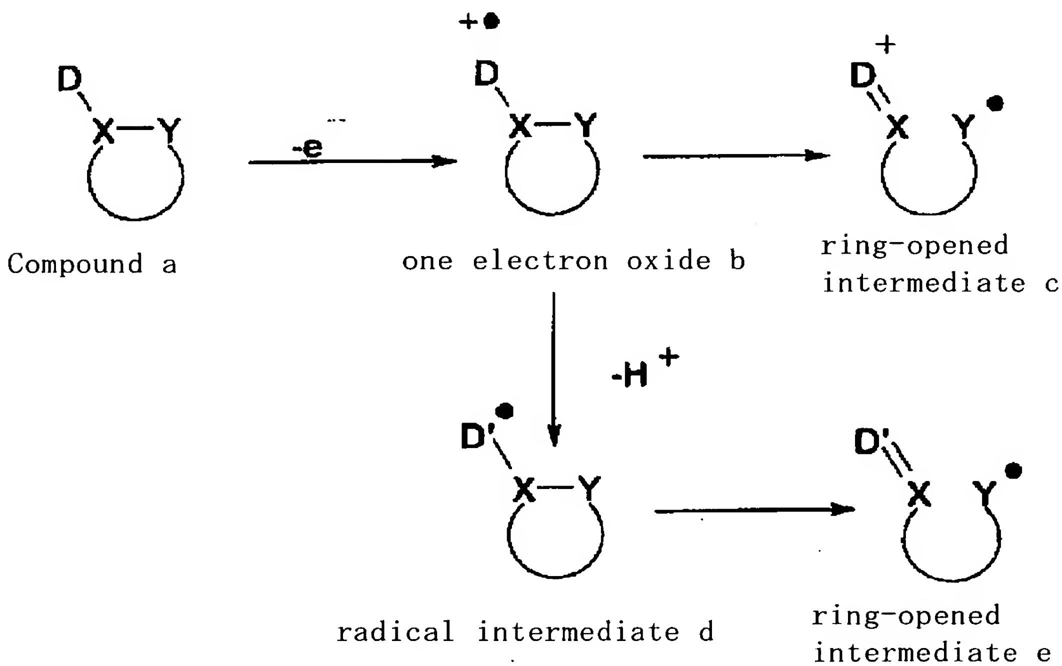
[0169]

Next, the compound of Type 4 will be described below.

The compound of Type 4 has a reducible group-substituted ring structure. After the reducible group is one-electron-oxidized, the compound can release further one or more electrons with a ring structure cleavage reaction. The ring cleavage reaction proceeds as follows.

[0170]

[F16]



[0171]

In the formula, compound *a* is the compound of Type 4. In compound *a*, D represents a reducible group, and X and Y each represent an atom forming a bond in the ring structure, which is cleaved after the one-electron oxidation. First, compound *a* is one-electron-oxidized to generate one-electron oxidation product b. Then, the X-Y bond is cleaved with conversion of the D-X single bond into a

double bond, whereby ring-opened intermediate c is provided. Alternatively, there is a case where one-electron oxidation product b is converted into radical intermediate d with deprotonation, and ring-opened intermediate e is provided in the same manner. Subsequently, further one or more electrons are released form thus-provided ring-opened intermediate c or e.

[0172]

The ring structure in the compound of Type 4 is a 3 to 7-membered, carbocyclic or heterocyclic, monocyclic or condensed, saturated or unsaturated, nonaromatic ring. The ring structure is preferably a saturated ring structure, more preferably 3- or 4-membered ring. Preferred examples of the ring structure include a cyclopropane ring, a cyclobutane ring, an oxirane ring, an oxetane ring, an aziridine ring, an azetidine ring, an episulphide ring and a thietane ring. More preferred are a cyclopropane ring, a cyclobutane ring, an oxirane ring, an oxetane ring and an azetidine ring, particularly preferred are a cyclopropane ring, a cyclobutane ring and an azetidine ring. The ring structure may have a substituent.

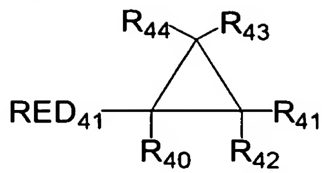
[0173]

The compound of Type 4 is preferably represented by the following general formula (E) or (F).

[0174]

[F17]

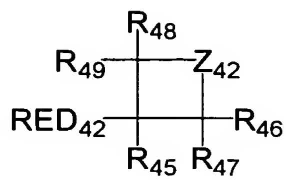
General formula (E)



[0175]

[F18]

General formula (F)



[0176]

In general formulae (E) and (F), RED_{41} and RED_{42} are the same as RED_{12} in general formula (B) with respect to the meanings and preferred embodiments, respectively. R_{40} to R_{44} and R_{45} to R_{49} each represent a hydrogen atom or a substituent. In general formula (F), Z_{42} represents $-CR_{420}R_{421}-$, $-NR_{423}-$, or -O-. R_{420} and R_{421} each represent a hydrogen atom or a substituent, and R_{423} represents a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group.

[0177]

In general formulae (E) and (F), each of R_{40} and R_{45} is preferably a hydrogen atom, an alkyl group or an aryl group, more preferably a hydrogen atom, an alkyl group or an aryl group. Each of R_{41} to R_{44} and R_{46} to R_{49} is preferably a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, an arylthio group, an alkylthio group, an acylamino group or a sulfoneamide

group, more preferably a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group,

[0178]

It is preferred that at least one of R_{41} to R_{44} is a donor group, and it is also preferred that both of R_{41} and R_{42}, or both of R_{43} and R_{44} are an electron-withdrawing group. It is more preferred that at least one of R_{41} to R_{44} is a donor group. It is furthermore preferred that at least one of R_{41} to R_{44} is a donor group and R_{41} to R_{44} other than the donor group are selected from a hydrogen atom and an alkyl group.

[0179]

A donor group referred to here is an "electron-donating group" or an aryl group substituted with at least one "electron-donating group." Preferable examples of donor groups include an alkylamino group, an arylamino group, a heterocyclicamino group, an electron-excessive aromatic heterocyclic group in a five-membered single ring or fused ring structure containing at least one nitrogen atom in a ring structure as part of the ring, a non-aromatic nitrogen containing hetrocyclic group having a nitrogen atom as a substitute and a phenyl group substituted with at least one electron-donating group. More preferable examples thereof include an alkylamino group, an aryamino group, an electron excessive aromatic heterocyclic group in a five-membered single ring or fused ring containing at least one nitrogen atom in a ring structure as a part (an indol ring, a pyrrole ring, a carbazole ring and the like), and a phenyl group substituted with an electron-donating group (a phenyl group substituted with three or more alkoxy

groups, a phenyl group substituted with a hydroxy group, an alkylamino group, or an arylamino group and the like). Particularly preferable examples thereof include an aryamino group, an electron excessive aromatic heterocyclic group in a five-membered single ring or fused ring containing at least one nitrogen atom in a ring structure as a part (especially, a 3-indolyl group), and a phenyl group substituted with an electron-donating group (especially, a trialkoxyphenyl group and a phenyl group substituted with an alkylamino group or an arylamino group).

[0180]

Z_{42} is preferably $-CR_{420}R_{421}-$ or $-NR_{423}-$, more preferably $-NR_{423}-$. Each of R_{420} and R_{421} is preferably a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an acylamino group or a sulfoneamino group, more preferably a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group. R_{423} is preferably a hydrogen atom, an alkyl group, an aryl group or an aromatic heterocyclic group, more preferably a hydrogen atom, an alkyl group or an aryl group.

[0181]

The substituent represented by each of R_{40} to R_{49}, R_{420}, R_{421} and R_{423} preferably has 40 or less carbon atoms, more preferably has 30 or less carbon atoms, particularly preferably 15 or less carbon atoms. The substituents of R_{40} to R_{49}, R_{420}, R_{421} and R_{423} may bond to each other or to the other portion such as RED_{41}, RED_{42} and Z_{42}, to form a ring.

[0182]

In the compounds of Types 1 to 4 used in the invention, the adsorptive group to the silver halide is such a group that is directly adsorbed on the silver halide or promotes adsorption of the compound onto the silver halide. Specifically, the adsorptive group is a mercapto group or a salt thereof; a thione group (-C(=S)-); a heterocyclic group containing at least one atom selected from the group consisting of a nitrogen atom, a sulfur atom, a selenium atom and a tellurium atom; a sulfide group; a cationic group; or an ethynyl group. Incidentally, the adsorptive group in the compound of Type 2 is not a sulfide group.

[0183]

The mercapto group or a salt thereof used as the adsorptive group may be a mercapto group or a salt thereof itself, and is more preferably a heterocyclic group, an aryl group or an alkyl group having a mercapto group or a salt thereof as a substituent. The heterocyclic group is a 5- to 7-membered, monocyclic or condensed, aromatic or nonaromatic, heterocyclic group. Examples thereof include an imidazole ring group, a thiazole ring group, an oxazole ring group, a benzimidazole ring group, a benzthiazole ring group, a benzoxazole ring group, a triazole ring group, a thiadiazole ring group, an oxadiazole ring group, a tetrazole ring group, a purine ring group, a pyridine ring group, a quinoline ring group, an isoquinoline ring group, a pyrimidine ring group, a triazine ring group, etc. The heterocyclic group may contain a quaternary nitrogen atom, and in this case, the mercapto group bonding to the heterocyclic group may be dissociated into a mesoion. Such heterocyclic group may be an imidazolium ring group, a pyrazolium ring group, a thiazolium ring group, a triazolium ring group, a tetrazolium ring group, a thiadiazolium ring group, a pyridinium ring group, a

pyrimidinium ring group, a triazinium ring group, etc. Preferred among them is a triazolium ring group such as a 1,2,4-triazolium-3-thiolate ring group. Examples of the aryl group include a phenyl group and a naphthyl group. Examples of the alkyl group include straight, branched or cyclic alkyl groups having 1 to 30 carbon atoms. When the mercapto group forms a salt, a counter ion of the salt may be a cation of an alkaline metal, an alkaline earth metal, a heavy metal, etc. such as Li^+, Na^+, K^+, Mg^{2+}, Ag^+ and Zn^{2+}; an ammonium ion; a heterocyclic group containing a quaternary nitrogen atom; a phosphonium ion; etc.

[0184]

Further, the mercapto group used as the adsorptive group may be tautomerized into a thione group. Specific examples of the thione group include a thioamide group (herein a -C(=S)-NH- group); and groups containing a structure of the thioamide group, such as linear or cyclic thioamide groups, a thiouredide group, a thiourethane group and a dithiocarbamic acid ester group. Examples of the cyclic thioamide group include a thiazolidine-2-thione group, an oxazolidine-2-thione group, a 2-thiohydantoin group, a rhodanine group, an isorhodanine group, a thiobarbituric acid group, a 2-thioxo-oxazolidine-4-one group, etc.

[0185]

The thione group used as the adsorbent group, as well as the thione group derived from the mercapto group by tautomerization, may be a linear or cyclic, thioamide, thiouredide, thiourethane or dithiocarbamic acid ester group that cannot be tautomerized into the mercapto group or has no hydrogen atom at α-position of the thione group.

[0186]

The heterocyclic group containing at least one atom selected from the group consisting of a nitrogen atom, a sulfur atom, a selenium atom and tellurium atom, which is used as the adsorbent group, is a nitrogen-containing heterocyclic group having a -NH- group that can form a silver imide (>NAg) as a moiety of the heterocycle; or a heterocyclic group having a -S- group, a -Se- group, a -Te- group or a =N- group that can form a coordinate bond with a silver ion as a moiety of the heterocycle. Examples of the former include a benzotriazole group, a triazole group, an indazole group, a pyrazole group, a tetrazole group, a benzimidazole group, an imidazole group, a purine group, etc. Examples of the latter include a thiophene group, a thiazole group, an oxazole group, a benzothiazole group, a benzoxazole group, a thiadiazole group, an oxadiazole group, a triazine group, a selenazole group, a benzselenazole group, a tellurazole group, a benztellurazole group, etc. The former is preferable.

[0187]

The sulfide group used as the adsorptive group may be any group with a -S- moiety, and preferably has a moiety of: alkyl or alkylene-S-alkyl or alkylene; aryl or arylene-S-alkyl or alkylene; or aryl or arylene-S-aryl or arylene. The sulfide group may form a ring structure, and may be a -S-S- group. Specific examples of the ring structure include groups with a thiolane ring, a 1,3-dithiolane ring, a 1,2-dithiolane ring, a thiane ring, a dithiane ring, a tetrahydro-1,4-thiazine ring (a thiomorpholine ring), etc. Particularly preferable as the sulfide groups are groups having a moiety of alkyl or alkylene-S-alkyl or alkylene.

[0188]

The cationic group used as the adsorptive group is a quaternary nitrogen-containing group, specifically a group with an ammonio group or a quaternary nitrogen-containing heterocyclic group. Incidentally, there is no case where the cationic group partly composes an atomic group forming a dye structure, such as a cyanine chromophoric group. The ammonio group may be a trialkylammonio group, a dialkylarylammonio group, an alkyldiarylammonio group, etc., and examples thereof include a benzyldimethylammonio group, a trihexylammonio group, a phenyldiethylammonio group, etc. Examples of the quaternary nitrogen-containing heterocyclic group include a pyridinio group, a quinolinio group, an isoquinolinio group, an imidazolio group, etc. Preferred are a pyridinio group and an imidazolio group, and particularly preferred is a pyridinio group. The quaternary nitrogen-containing heterocyclic group may have an optional substituent. Preferred as the substituent in the case of the pyridinio group and the imidazolio group are alkyl groups, aryl groups, acylamino groups, a chlorine atom, alkoxycarbonyl groups and carbamoyl groups. Particularly preferred as the substituent in the case of the pyridinio group is a phenyl group.

[0189]

The ethynyl group used as the adsorptive group means a -C≡CH group, in which the hydrogen atom may be substituted.

The adsorptive group may have an optional substituent.

[0190]

Specific examples of the adsorptive group further include groups described in pages 4 to 7 of a specification of JP-A No. 11-95355.

[0191]

Preferred as the adsorptive group used in the invention are mercapto-substituted, nitrogen-containing, heterocyclic groups such as a 2-mercaptothiadiazole group, a 3-mercapto-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercapto-1,3,4-oxadiazole group, a 2-mercaptobenzoxazole group, a 2-mercaptobenzthiazole group and a 1,5-dimethyl-1,2,4-triazolium-3-thiolate group; and nitrogen-containing heterocyclic groups having a -NH- group that can form a silver imide (>NAg) as a moiety of the heterocycle, such as a benzotriazole group, a benzimidazole group and an indazole group. Particularly preferred are a 5-mercaptotetrazole group, a 3-mercapto-1,2,4-triazole group and a benzotriazole group, and the most preferred are a 3-mercapto-1,2,4-triazole group and a 5-mercaptotetrazole group.

[0192]

Among these compounds, it is particularly preferred that the compound has two or more mercapto groups as a moiety. The mercapto group (-SH) may be converted into a thione group in the case where it can be tautomerized. The compound may have two or more adsorbent groups containing above-mentioned mercapto or thione group as a moiety, such as a cyclic thioamide group, an alkylmercapto group, an arylmercapto group and a heterocyclic mercapto group. Further, the compound may have one or more adsorptive group containing two or more mercapto or thione groups as a moiety, such as a dimercapto-substituted,

nitrogen-containing, heterocyclic group.

[0193]

Examples of the adsorptive group containing two or more mercapto group, such as a dimercapto-substituted, nitrogen-containing, heterocyclic group, include a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, a 3,5-dimercapto-1,2,4-triazole group, a 2,5-dimercapto-1,3-thiazole group, a 2,5-dimercapto-1,3-oxazole group, a 2,7-dimercapto-5-methyl-*s*-triazolo(1,5-A)-pyrimidine group, a 2,6,8-trimercaptopurine group, a 6,8-dimercaptopurine group, a 3,5,7-trimercapto-*s*-triazolotriazine group, a 4,6-dimercaptopyrazolo pyrimidine group, a 2,5-dimercapto-imidazole group, etc. Particularly preferred are a 2,4-dimercaptopyrimidine group, a 2,4-dimercaptotriazine group, and a 3,5-dimercapto-1,2,4-triazole group.

[0194]

The adsorptive group may be connected to any position of the compound represented by each of general formulae (A) to (F) and (1) to (3). Preferred portions, which the adsorptive group bonds to, are RED_{11}, RED_{12}, RED_2 and RED_3 in general formulae (A) to (D), RED_{41}, R_{41}, RED_{42}, and R_{46} to R_{48} in general formulae (E) and (F), and optional portions other than R_1, R_2, R_{11}, R_{12}, R_{31}, L_1, L_{21} and L_{31} in general formulae (1) to (3). Further, more preferred portions are RED_{11} to RED_{42} in general formulae (A) to (F).

[0195]

The spectral sensitizer moiety is a group containing a spectral sensitizer

chromophore, a residual group provided by removing an optional hydrogen atom or substituent from a spectral sensitizer compound. The spectral sensitizer moiety may be connected to any position of the compound represented by each of general formulae (A) to (F) and (1) to (3). Preferred portion, which the spectral sensitizer moiety bonds to, are RED_{11}, RED_{12}, RED_2 and RED_3 in general formulae (A) to (D), RED_{41}, R_{41}, RED_{42}, and R_{46} to R_{48} in general formulae (E) and (F), and optional portions other than R_1, R_2, R_{11}, R_{12}, R_{31}, L_1, L_{21} and L_{31} in general formulae (1) to (3). Further, more preferred portions are RED_{11} to RED_{42} in general formulae (A) to (F). The spectral sensitizer is preferably such that typically used in color sensitizing techniques. Examples thereof include cyanine dyes, composite cyanine dyes, merocyanine dyes, composite merocyanine dyes, homopolar cyanine dyes, styryl dyes, and hemicyanine dyes. Typical spectral sensitizers are disclosed in Research Disclosure, Item 36544, September 1994. The dyes can be synthesized by one skilled in the art according to procedures described in the above Research Disclosure and F. M. Hamer, *The Cyanine dyes and Related Compounds*, Interscience Publishers, New York, 1964. Further, dyes described in pages 4 to 7 of a specification of JP-A No. 11-95355 (USP No. 6,054,260) may be used in the invention.

[0196]

The compounds of Types 1 to 4 used in the invention has preferably 10 to 60 carbon atoms in total, more preferably 15 to 50 carbon atoms, furthermore preferably 18 to 40 carbon atoms, particularly preferably 18 to 30 carbon atoms.

[0197]

When a silver halide photosensitive material using the compounds of Types 1 to 4 is exposed, the compound is one-electron-oxidized. After the subsequent reaction, the compound is further oxidized while releasing one electron, or two or more electrons depending on Type. An oxidation potential in the first one-electron oxidation is preferably 1.4 V or less, more preferably 1.0 V or less. This oxidation potential is preferably 0 V or more, more preferably 0.3 V or more. Thus, the oxidation potential is preferably approximately 0 V to 1.4 V, more preferably approximately 0.3 V to 1.0 V.

[0198]

The oxidation potential may be measured by a cyclic voltammetry technique. Specifically, a sample is dissolved in a solution of acetonitrile/water containing 0.1 M lithium perchlorate = 80/20 (volume %), nitrogen gas is passed through the resultant solution for 10 minutes, and then the oxidation potential is measured at 25 °C at a potential scanning rate of 0.1 V/second by using a glassy carbon disk as a working electrode, using a platinum wire as a counter electrode, and using a calomel electrode (SCE) as a reference electrode. The oxidation potential per SCE is obtained at peak potential of cyclic voltammetric curve.

[0199]

In the case where the compound of Types 1 to 4 is one-electron-oxidized and release further one electron after the subsequent reaction, an oxidation potential in the subsequent oxidation is preferably -0.5 V to –2 V, more preferably -0.7 V to –2 V, furthermore preferably -0.9 V to -1.6 V.

[0200]

In the case where the compound of Types 1 to 4 is one-electron-oxidized and release further two or more electrons after the subsequent reaction, oxidation potentials in the subsequent oxidation are not particularly limited. The oxidation potentials in the subsequent oxidation often cannot be measured precisely, because an oxidation potential in releasing the second electron cannot be clearly differentiated from an oxidation potential in releasing the third electron.

[0201]

Next, the compound of Type 5 will be described.

The compound of Type 5 is represented by X-Y, in which X represents a reducible group and Y represents a leaving group. The reducible group represented by X can be one-electron-oxidized to provide a one-electron oxidation product, which can be converted into an X radical by eliminating the leaving group of Y with a subsequent X-Y bond cleavage reaction. The X radical can release further one electron. The oxidation reaction of the compound of Type T5 may be represented by the following formula.

[0202]

[F19]

$$\mathrm{X{-}Y} \xrightarrow{\text{oxidize}(-e^-)} (\mathrm{X{-}Y})^{+\bullet} \xrightarrow{\text{split}} \mathrm{X}\bullet + \mathrm{Y}^+ \xrightarrow{\text{one electron release}(-e^-)} \mathrm{X}^+$$

[0203]

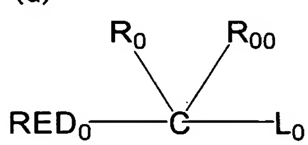
The compound of Type 5 exhibits an oxidation potential of preferably 0 V to 1.4 V, more preferably 0.3 V to 1.0 V. The radical X· generated in the formula exhibits an oxidation potential of preferably -0.7 V to -2.0 V, more preferably -0.9 V to -1.6 V.

[0204]

The compound of Type 5 is preferably represented by the following general formula (G).

[0205] [F20]

General formula (G)



[0206]

In general formula (G), RED_0 represents a reducible group, L_0 represents a leaving group, and R_0 and R_{00} each represent a hydrogen atom or a substituent. RED_0 and R_0, and R_0 and R_{00} may be bond together to form a ring structure, respectively. RED_0 is the same as RED_2 in general formula (C) with respect to the meanings and preferred embodiments. R_0 and R_{00} are the same as R_{21} and R_{22} in general formula (C) with respect to the meanings and preferred embodiments, respectively. Incidentally, R_0 and R_{00} are not the same as the leaving group of L_0 respectively, except for a hydrogen atom. RED_0 and R_0 may bond together to form a ring structure with examples and preferred embodiments the same as those of the ring structure formed by bonding RED_2 and R_{21} in general formula (C).

Examples of the ring structure formed by bonding R_0 and R_{00} each other include a cyclopentane ring, a tetrahydrofuran ring, etc. In general formula (G), L_0 is the same as L_2 in general formula (C) with respect to the meanings and preferred embodiments.

[0207]

The compound represented by general formula (G) preferably has an adsorptive group to the silver halide or a spectrally sensitizing dye moiety. However, the compound does not have two or more adsorptive groups when L_0 is a group other than a silyl group. Incidentally, the compound may have two or more sulfide groups as the adsorbent groups, not depending on L_0.

[0208]

The adsorptive group to the silver halide in the compound represented by general formula (G) may be the same as those in the compounds of Types 1 to 4, and further may be the same as all of the compounds and preferred embodiments described as "an adsorptive group to the silver halide" in pages 4 to 7 of a specification of JP-A No. 11-95355.

The spectral sensitizer moiety in the compound represented by general formula (G) is the same as in the compounds of Types 1 to 4, and may be the same as all of the compounds and preferred embodiments described as "photoabsorptive group" in pages 7 to 14 of a specification of JP-A No. 11-95355.

[0209]

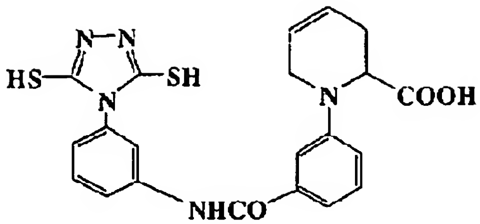
Specific examples of the compounds of Types 1 to 5 used in the invention

are illustrated below without intention of restricting the scope of the invention.

[0210]

[F21]

1



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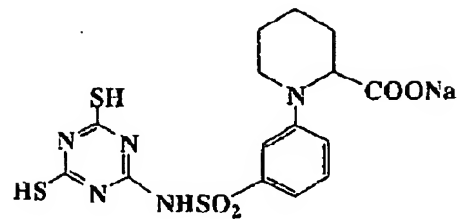

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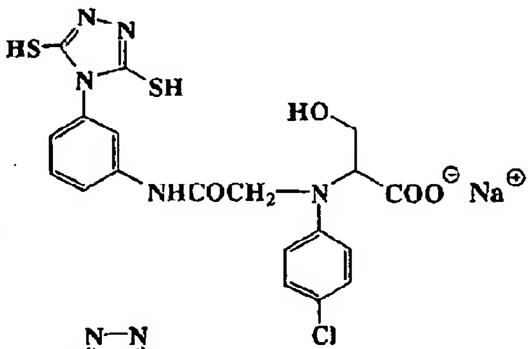

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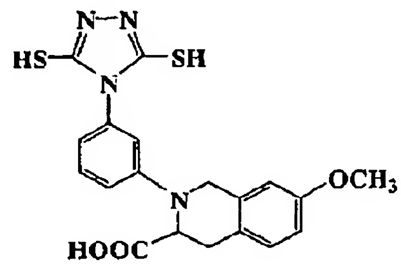

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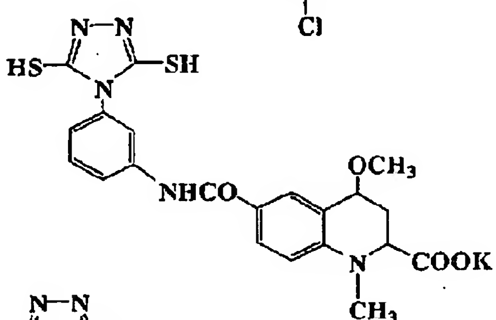

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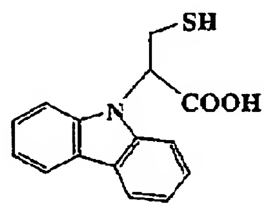

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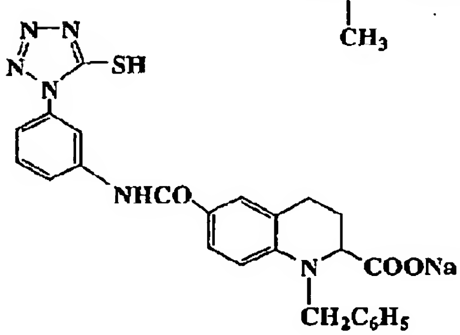

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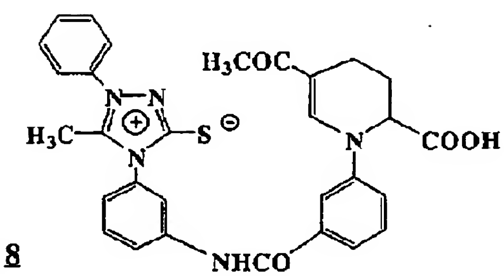

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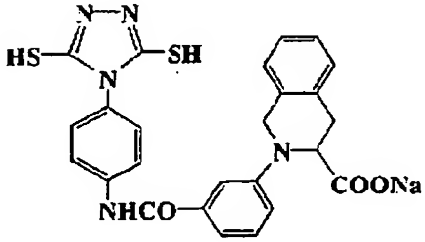

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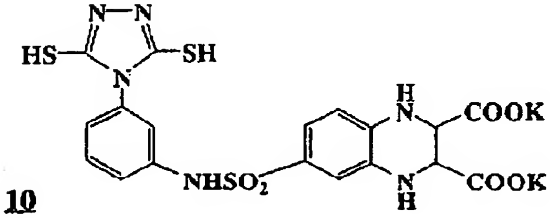
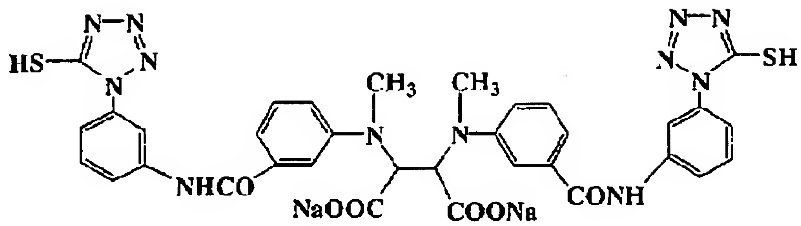


[0211]

[F22]



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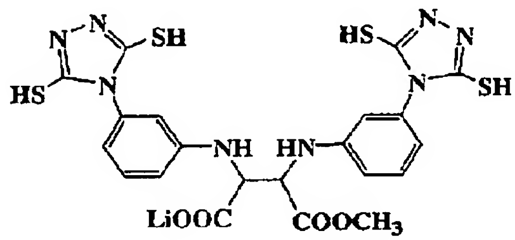

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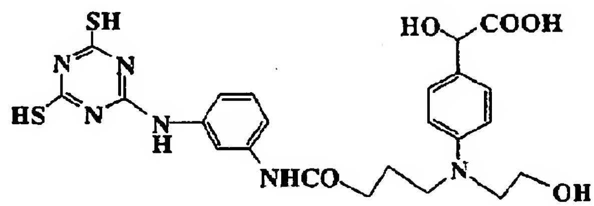

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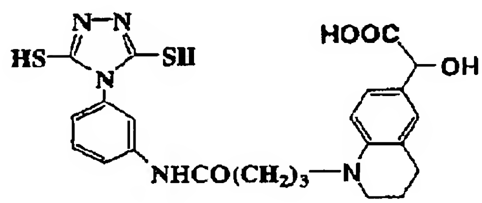

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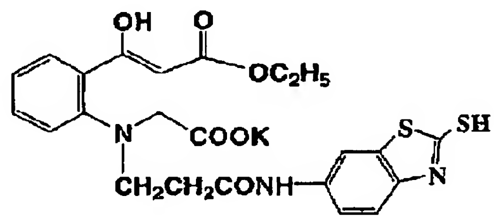

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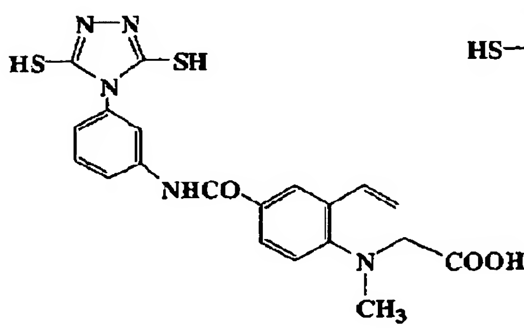

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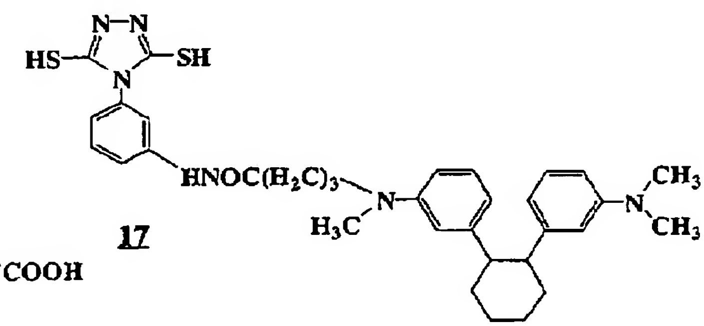

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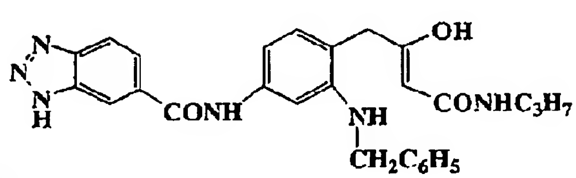

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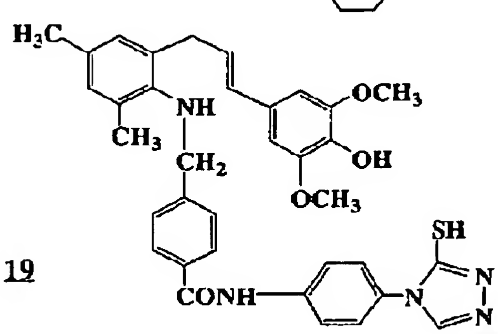

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[0212]

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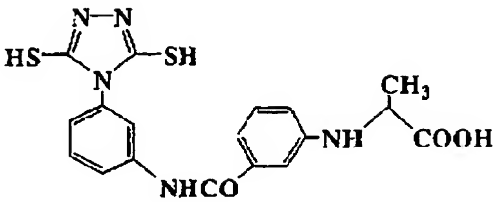

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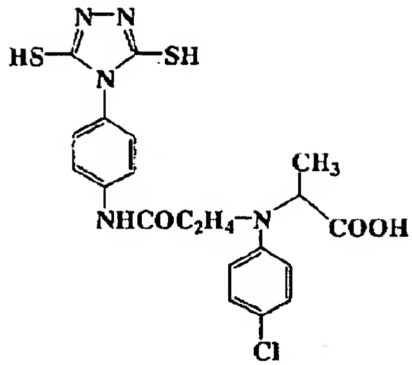

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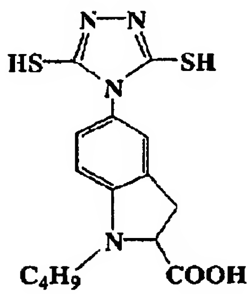

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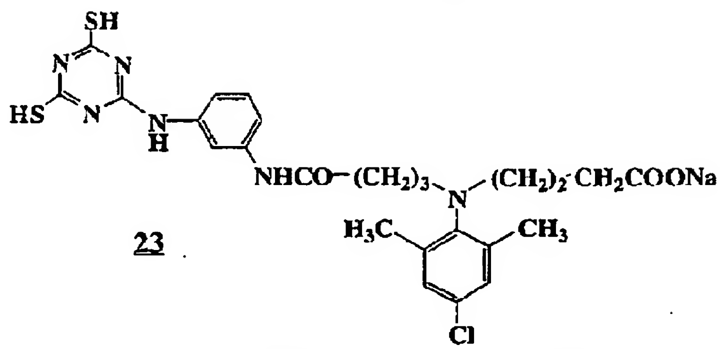

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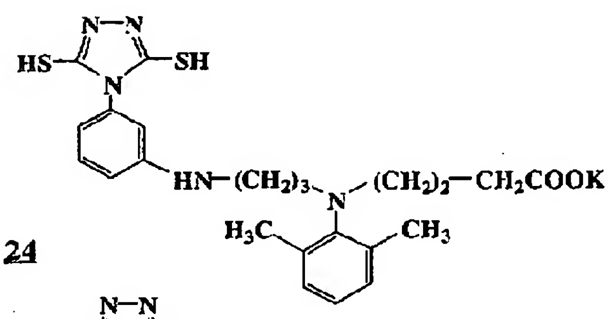

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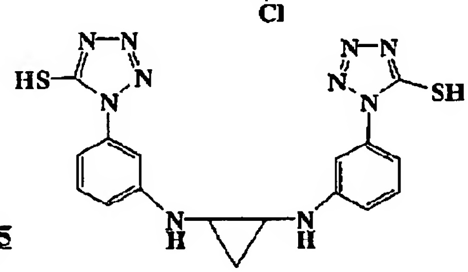

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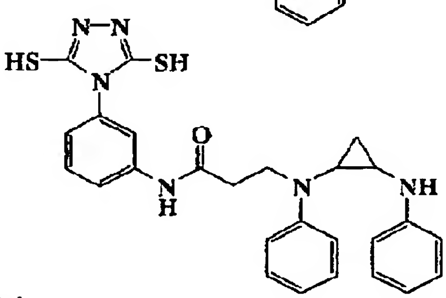

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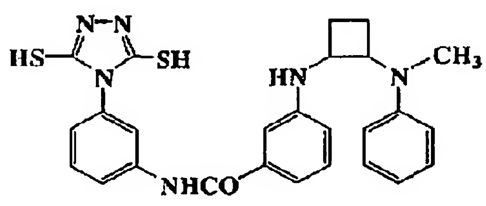

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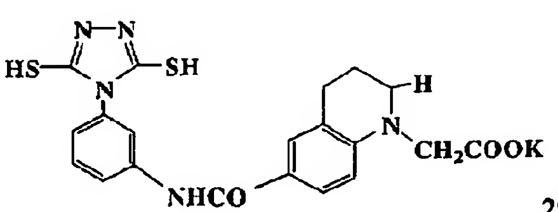

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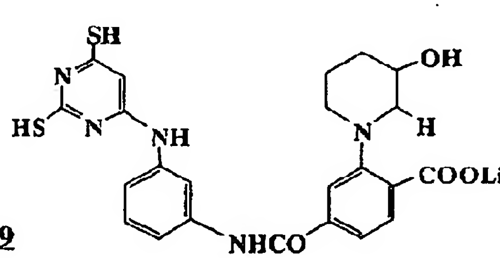

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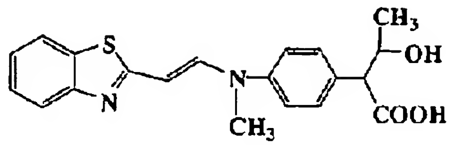

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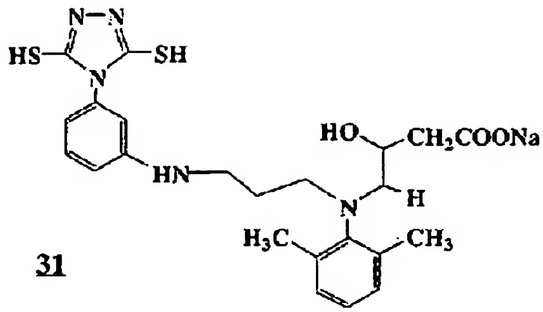

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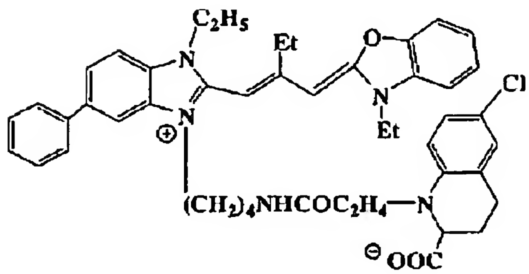

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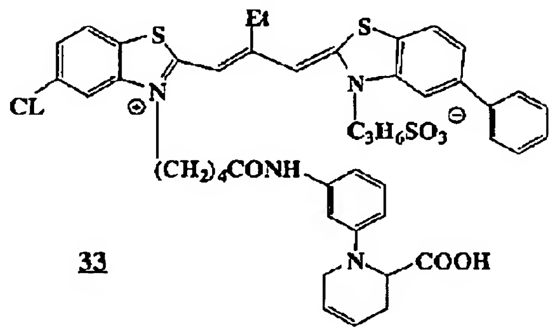

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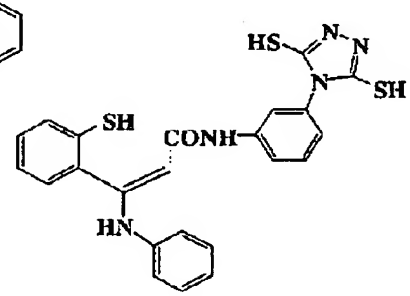

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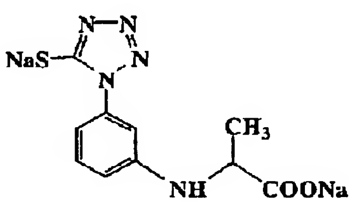

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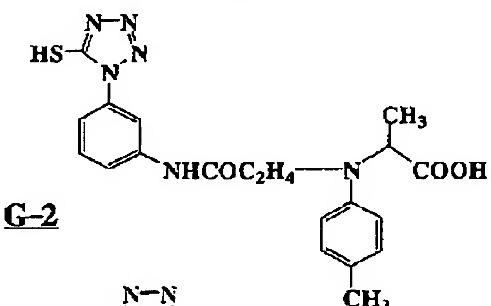

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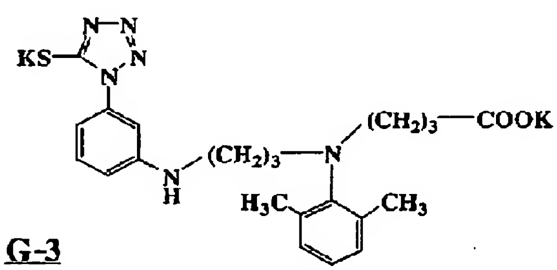

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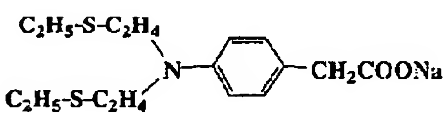

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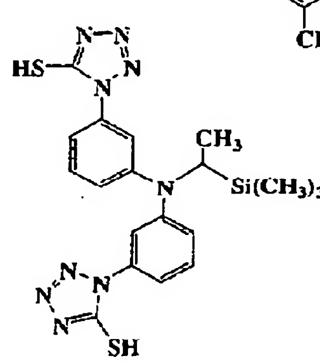


G-5

[0214]

The compounds of Types 1 to 4 used in the invention are the same as compounds described in detail in Japanese Patent Application Nos. 2002-192373, 2002-188537, 2002-188536, 2001-272137 and 2002-192374, respectively. The specific examples of the compounds of Types 1 to 4 used in the invention further include compound examples disclosed in the specifications. Synthesis examples of the compounds of Types 1 to 4 used in the invention may be the same as described in the specifications.

[0215]

Specific examples of the compound represented by general formula (G) further include examples of compound referred to as "one photon two electrons sensitizer" or "deprotonating electron-donating sensitizer" described in JP-A No. 9-211769 (Compound PMT-1 to S-37 in Tables E and F, pages 28 to 32); JP-A No. 9-211774; JP-A No. 11-95355 (Compound INV 1 to 36); JP-W No. 2001-500996 (Compound 1 to 74, 80 to 87, and 92 to 122); USP Nos. 5747235 and 5747236; EP No. 786692 A1 (Compound INV 1 to 35); EP No. 893732 A1; USP Nos. 6054260 and 5994051; etc.

[0216]

The compounds of Types 1 to 5 may be used at any time during preparation of the photosensitive silver halide emulsion and production of the photothermographic material. For example, the compound may be used, in a photosensitive silver halide grain formation step, in a desalting step, in a chemical sensitization step, before application, etc. The compound may be added in

several times, during these steps. The compound is preferably added, after the photosensitive silver halide grain formation step and before the desalting step; in the chemical sensitization step (just before the chemical sensitization to immediately after the chemical sensitization); or before the application. The compound is more preferably added, just before the chemical sensitization step to before mixing with the non-photosensitive organic silver salt.

[0217]

It is preferred that the compound of Types 1 to 5 used in the invention is dissolved in water, a water-soluble solvent such as methanol and ethanol, or a mixed solvent thereof, to be added. In the case where the compound is dissolved in water and solubility of the compound is increased by increasing or decreasing a pH value of the solvent, the pH value may be increased or decreased to dissolve and add the compound.

[0218]

The compound of Types 1 to 5 used in the invention is preferably added to the image forming layer comprising the photosensitive silver halide and the non-photosensitive organic silver salt. The compound may be added to a surface protective layer, an intermediate layer, as well as the image forming layer comprising the photosensitive silver halide and the non-photosensitive organic silver salt, to be diffused to the image forming layer in the application step. The compound may be added before or after addition of a sensitizing dye. A mol value of the compound per one mol of the silver halide is preferably 1×10^{-9} mol to 5×10^{-1} mol, more preferably 1×10^{-8} mol to 5×10^{-2} mol, in a layer comprising

the photosensitive silver halide emulsion.

[0219]

1) Sensitizing dye

In the invention, as sensitizing dyes that are used for applying for the invention, can be selected such sensitizing dyes as those that sensitize spectrally silver halide grains in preferable range of wavelength when they are adsorbed by silver halogen grains, and furthermore have spectral sensitivity suitable for spectral characteristics of light source for exposure. It is preferable that the photothermographic material of the present invention is spectrally sensitized so as to have a peak of spectral sensitivity particularly within a range of 600 nm to 900 nm or within a range of 300 nm to 500 nm. The known sensitizing dyes and methods for adding the dyes are described in: JP-A No. 11-65021, paragraphs 0103 to 0109; JP-A No. 10-186572, compounds represented by general formula (II); JP-A No. 11-119374, dyes represented by general formula (I) and paragraph 0106; USP No. 5510236; USP No. 3871887, dyes described in Example 5; JP-A No. 2-96131; JP-A No. 59-48753, dyes disclosed therein; EP 0803764A1, page 19, line 38 to page 20, line 35; Japanese Patent Application Nos. 2000-86865, 2000-102560 and 2000-205399; etc. These sensitizing dyes may be used singly or in combination of two or more thereof.

[0220]

The amount of sensitizing dye in the present invention can be controlled in accordance with sensitivity and fogging performance thereof. However, the amount is preferably 10^{-6} to 1 mol per one mol of silver halide of the

photosensitive layer, and more particularly 10^{-4} to 10^{-1} mol per one mol.

[0221]

A supersensitizer may be used in the invention to increase spectral sensitization efficiency. Examples of the supersensitizer used in the invention include compounds disclosed in EP-A No. 587,338; USP Nos. 3877943 and 4873184; JP-A Nos. 5-341432, 11-109547 and 10-111543; and the like.

[0222]

11) Combined use of silver halides

The photosensitive silver halide emulsion in the photosensitive material used in the invention may be used alone, or two or more kinds of them (for example, those of different average particle sizes, different halogen compositions, different crystal habits and of different conditions for chemical sensitization) may be used together. Gradation can be controlled by using plural kinds of photosensitive silver halides of different sensitivity. The relevant techniques can include those described, for example, in JP-A Nos. 57-119341, 53-106125, 47-3929, 48-55730, 46-5187, 50-73627, and 57-150841. It is preferred to provide a sensitivity difference of 0.2 or more in terms of log E between each of the emulsions.

[0223]

12) Mixture of silver halide and organic silver salt

Organic silver salts are prepared by adding alkali metal salts (e.g., sodium hydroxide, potassium hydroxide) to organic acids to convert at least a part of the

organic acids into alkali metal soap of the organic acids, and then by adding thereto a water-soluble silver salt (e.g., silver nitrate). Photosensitive silver halides may be added at any stage in the process of preparing the organic silver salts. As main mixing processes, there are (A) a process in which silver halides are added to organic acids in advance, admixed with alkali metal salts, and then admixed with a water-soluble silver salt; (B) a process in which alkali metal soap prepared from organic acids is mixed with silver halides, and thereto a water-soluble silver salt is added; (C) a process in which alkali metal soap is prepared from organic acids, a part thereof is converted into the silver salt, and then silver halides are added thereto, and further the remaining part is converted into the silver salt; and (D) a process in which organic silver salts are formed, and then mixed with silver halides. Of these processes, (B) and (C) are preferred over the others.

[0224]

As for (B) and (C), the photosensitive silver halide is formed under the absence of the non-photosensitive organic silver salt and then mixed in the process for preparing the organic silver salt. This is because a sufficient sensitivity can not sometimes be attained by the method of forming the silver halide by adding a halogenating agent to the organic silver salt.

As for (D), the method of mixing the silver halide and the organic silver salt can include a method of mixing a separately prepared photosensitive silver halide and an organic silver salt by a high speed stirrer, ball mill, sand mill, colloid mill, vibration mill, or homogenizer, or a method of mixing a photosensitive silver halide completed for preparation at any timing in the preparation of an organic

silver salt and preparing the organic silver salt. The effect of the invention can be obtained preferably by any of the methods described above.

[0225]

The organic silver salt including the silver halide is preferably in the form of fine particle dispersion. For the method to disperse in fine particle, a high speed stirrer, ball mill, sand mill, colloid mill, vibration mill, or a high pressure homogenizer can be used.

[0226]

13) Mixture of silver halide into coating solution

In the invention, the time of adding silver halide to the coating solution for the image forming layer is preferably in the range from 180 minutes before to just prior to the coating, more preferably, 60 minutes before to 10 seconds before coating. But there is no restriction for mixing method and mixing condition as far as the effect of the invention appears sufficient. As an embodiment of a mixing method, there is a method of mixing in the tank controlling the average residence time to be desired. The average residence time herein is calculated from addition flux and the amount of solution transferred to the coater. And another embodiment of mixing method is a method using a static mixer, which is described in 8th edition of "Ekitai kongou gijutu" by N.Harnby and M.F.Edwards, translated by Kouji Takahashi (Nikkankougyou shinbunsya, 1989).

[0227]

3. Reducing agent

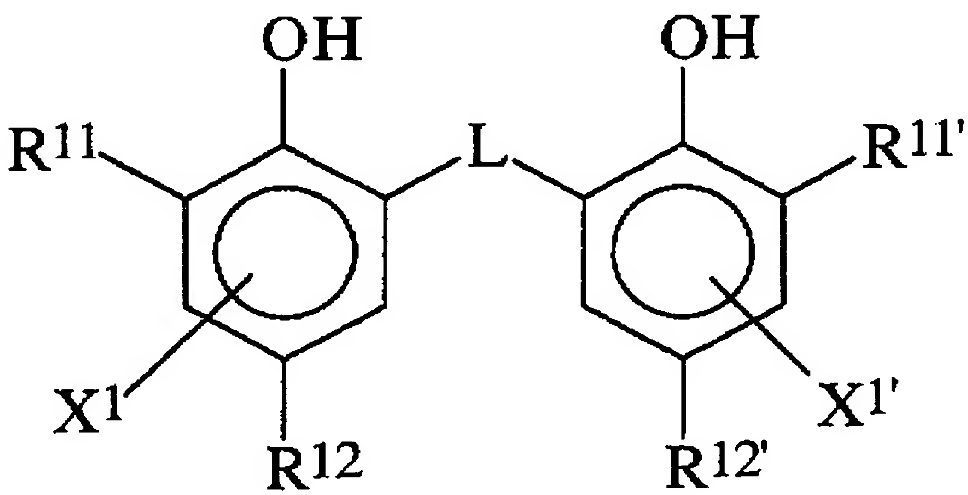
The reducing agent used in the invention is the compound that is capable of reducing a silver ion to form a developed silver at a thermal developing process.

As a reducing agent used in the invention, the compound represented by the following formula (R) is preferred. These compounds are illustrated below in detail.

[0228]

[F25]

General Formura (R)



[0229]

In formula (R), R^{11} and $R^{11'}$ each independently represent an alkyl group having 1 to 20 carbon atoms. R^{12} and $R^{12'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. L represents a -S- group or a -CHR^{13}- group. R^{13} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms. X and X^1 each

independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.

[0230]

Each of the substituents is to be described specifically.

1) R^{11} and $R^{11'}$

R^{11} and $R^{11'}$ each independently represent a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms. The substituent for the alkyl group has no particular restriction and can include, preferably, aryl group, hydroxy group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, acyl group, carbamoyl group, ester group, and halogen atom.

[0231]

2) R^{12} and $R^{12'}$, X and X^1

R^{12} and $R^{12'}$ each independently represent a hydrogen atom or a group capable of substituting for a hydorgen atom on a benzene ring.

X and X^1 each independently represent a hydrogen atom or a group capable of substituting for a hydorgen atom on a benzene ring. Each of the groups capable of substituting for a hydrogen atom on the benzene ring can include, preferably, alkyl group, aryl group, halogen atom, alkoxy group, and acylamino group.

[0232]

3) L

L represents a -S- group or a $-CHR^{13}-$ group. R^{13} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms in which the alkyl group may have a substituent.

[0233]

Specific examples of the non-substituted alkyl group for R^{13} can include, for example, methyl group, ethyl group, propyl group, butyl group, heptyl group, undecyl group, isopropyl group, 1-ethylpentyl group, and 2,4,4-trimethylpentyl group.

Examples of the substituent for the alkyl group can include, like substituent R^{11}, a halogen atom, an alkoxy group, alkylthio group, aryloxy group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, oxycarbonyl group, carbamoyl group, and sulfamoyl group.

[0234]

4) Preferred substituents

R^{11} and $R^{11'}$ are, preferably, a secondary or tertiary alkyl group having 3 to 15 carbon atoms and can include, specifically, isopropyl group, isobutyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, cyclopentyl group, 1-methylcyclohexyl group, and 1-methylcyclopropyl group. R^{11} and $R^{11'}$ each represents, more preferably, tertiary alkyl group having 4 to 12 carbon atoms and, among them, t-butyl group, t-amyl group, 1-methylcyclohexyl group are further preferred, t-butyl group being most preferred.

[0235]

R^{12} and $R^{12'}$ are, preferably, alkyl groups having 1 to 20 carbon atoms and can include, specifically, methyl group, ethyl group, propyl group, butyl group, isopropyl group, t-butyl group, t-amyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, methoxymethyl group and methoxyethyl group. More preferred are methyl group, ethyl group, propyl group, isopropyl group, and t-butyl group.

[0236]

X and X^1 are, preferably, a hydrogen atom, halogen atom, or alkyl group, and more preferably, hydrogen atom.

[0237]

L is preferably a group $-CHR^{13}-$.

[0238]

R^{13} is, preferably, a hydrogen atom or an alkyl group having 1 to 15 carbon atoms. The alkyl group is preferably methyl group, ethyl group, propyl group, isopropyl group and 2,4,4-trimethylpentyl group. Particularly preferred R^{13} is a hydrogen atom, methyl group, propyl group or isopropyl group.

[0239]

In a case where R^{13} is a hydrogen atom, R^{12} and $R^{12'}$ each represent, preferably, an alkyl group having 2 to 5 carbon atoms, ethyl group and propyl group being more preferred and ethyl group being most preferred.

[0240]

In a case where R^{13} is a primary or secondary alkyl group having 1 to 8 carbon atoms, R^{12} and $R^{12'}$ each represent preferably methyl group. As the primary or secondary alkyl group of 1 to 8 carbon atoms for R^{13}, methyl group, ethyl group, propyl group and isopropyl group are more preferred, and methyl group, ethyl group, and propyl group are further preferred.

[0241]

In a case where each of R^{11}, $R^{11'}$ and R^{12}, $R^{12'}$ is methyl group, R^{13} is preferably a secondary alkyl group. In this case, the secondary alkyl group for R^{13} is preferably isopropyl group, isobutyl group and 1-ethylpentyl group, with isopropyl group being more preferred.

[0242]

The reducing agent described above show various different thermal developing performances depending on the combination of R^{11}, $R^{11'}$ and R^{12}, $R^{12'}$, as well as R^{13}. Since the thermal developing performances can be controlled by using two or more kinds of reducing agents at various mixing ratios, it is preferred to use two or more kinds of reducing agents in combination depending on the purpose.

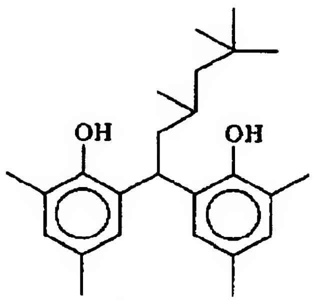
[0243]

Specific examples of the compounds represented by formula (R) according to the invention are shown below but the invention is not restricted to them.

[0244]

[F26]

(I－1)



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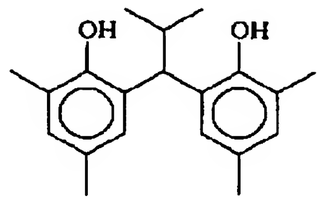

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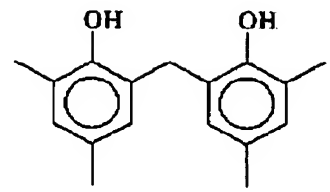

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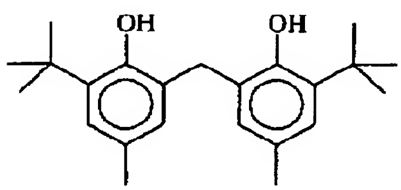

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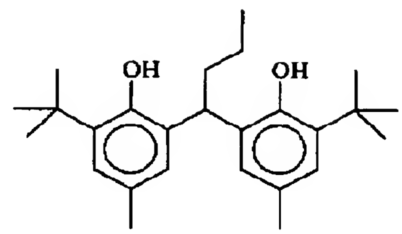

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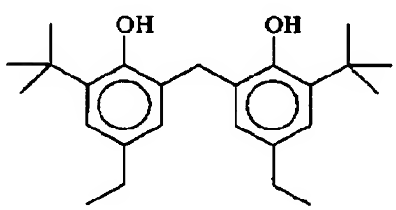

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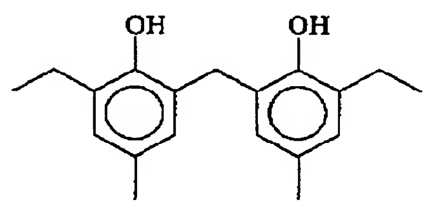

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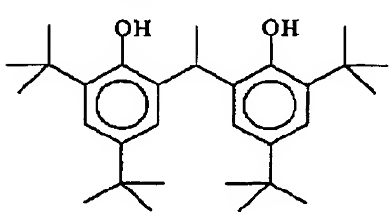

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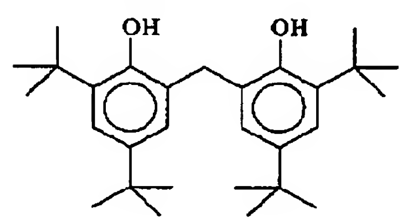

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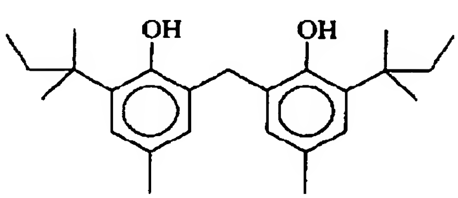

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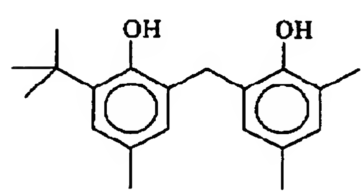
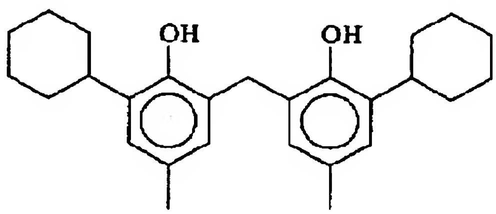


[0245]

[F27]

(I－12)



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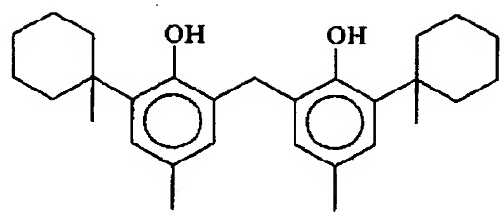

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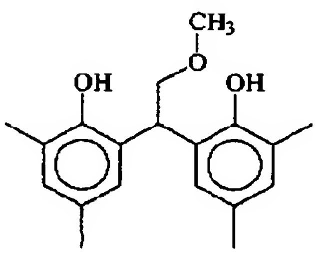

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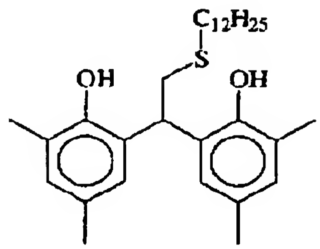

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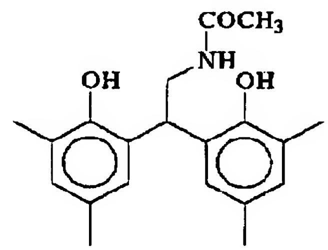

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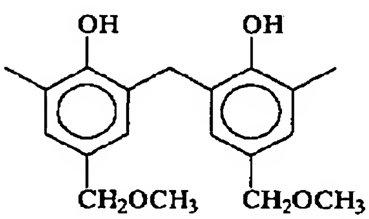

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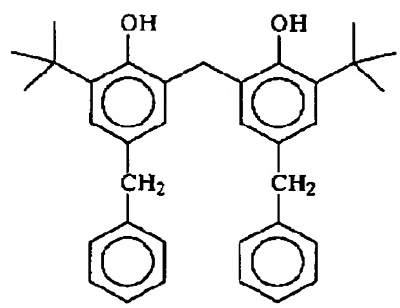

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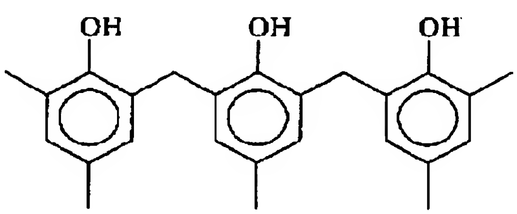

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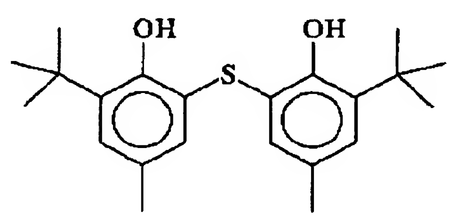


[0246]

In the invention, the addition amount of the reducing agent is, preferably, from 0.01 g/m^2 to 5.0 g/m^2, and more preferably, 0.1 g/m^2 to 3.0 g/m^2. It is, preferably, contained by 5 mol% to 50 mol%, and more preferably, 10 mol% to 40 mol% per one mole of silver in the image forming layer.

[0247]

The reducing agent of the invention is preferably contained in the image forming layer containing an organic silver salt and a photosensitive silver halide and the layer adjacent to the image forming layer, however it is more preferably contained in the image forming layer.

[0248]

In the invention, the reducing agent may be incorporated into photosensitive material by being added into the coating solution, such as in the form of a solution, an emulsion dispersion, a solid particle dispersion, and the like. It is particularly preferable to add the reducing agent in the form of a solution, where the reducing agent is solved in the coating solution or in the organic solvent which is miscible with the coating solution.

[0249]

4. Non-photosensitive organic silver salt

The non-photosensitive organic silver salt particle according to the invention is relatively stable to light but serves as to supply silver ions and forms

silver images when heated to 80°C or higher under the presence of an exposed photosensitive silver halide and a reducing agent. The organic silver salt may be any organic material containing a source capable of reducing silver ions. Such non-photosensitive organic silver salt is disclosed, for example, in JP-A No. 10-62899 (paragraph Nos. 0048 to 0049), EP-A No. 0803764 A1 (page 18, line 24 to page 19, line 37), EP-A No. 0962812 A1, JP-A Nos. 11-349591, 2000-7683, and 2000-72711, and the like. A silver salt of organic acid, particularly, a silver salt of long chained fatty acid carboxylic acid (number of carbon atoms having 10 to 30, preferably, 15 to 28) is preferable. Preferred examples of the silver salt of the organic acid can include, for example, silver behenate, silver arachidinic acid, silver stearate, silver oleate, silver laurate, silver capronate, silver myristate, silver palmitate and mixtures thereof. In the present invention, among the organic silver salts, an organic silver salt with the silver behenate content of 30 mol% to 80 mol% is used. Particularly, it is preferred that the silver behenate content is 40 mol% to 70 mol%. For the remaining organic silver salt, a silver salt of a long chained fatty carboxylic acid is preferred, more preferably, a silver salt of long chained fatty carboxylic acid having 10 to 30 carbon atoms, and particularly preferably, a silver salt of long chained fatty carboxylic acid having 15 to 28 carbon atoms.

[0250]

There is no particular restriction on the shape of the organic silver salt usable in the invention and it may cubic, cuboid, bar-like, needle-like, plate-like or flaky shape. Among them, a cubic, cuboid, bar-like, needle-like shaped organic silver salt is relatively preferred. A cubic, cuboid, bar-like, needle-like shaped

organic silver salt is defined as shown below. An organic acid silver salt is observed under an electron microscope, calculation is made while approximating the shape of an organic acid silver salt particle to a rectangular body and assuming each side of the rectangular body as a, b, c from the shorter side ($a \leqq b \leqq c$). The particle which satisfies the relation: $0.9 \leqq a/c \leqq 1.0$ is defined as a cubic shape. The particle which satisfies the relation: $0.2 \leqq a/c < 0.9$ and $0.2 \leqq b/c < 1.0$ is defined as a cuboid shape. The particle which satisfies the relation: $0.1 \leqq a/c < 0.2$ and $0.1 \leqq b/c < 0.3$ is defined as a bar-like shape. The particle which satisfies the relation: $a/c < 0.1$ and $b/c < 0.1$ is defined as a needle-like shape. In the invention, more preferableshape of the organic silver salt is a bar-like shape or a needle-like shape, amd most preferred is a needle-like shape.

[0251]

It is preferable to decrease the size of organic silver. In the filed of a silver halide photosensitive material, the inverse proportion between the size and covering power of a silver salt particle is well known. This relation is observed also in the photothermographic material of the invention, and it means that when the size of an organic silver particle in the image forming layer is large, the covering power decreases and image density becomes low. In the present invention, it is preferable that the short axis is 0.01 μm to 0.20 μm, the long axis is 0.10 μm to 5.0 μm, and it is more preferable that the short axis is 0.01 μm to 0.15 μm, the long axis is 0.10 μm to 4.0 μm. As the particle size distribution of the organic silver salt, mono-dispersion is preferred. In the mono-dispersion, the percentage for the value obtained by dividing the standard deviation for the length of minor axis and major axis by the minor axis and the major axis respectively is,

preferably, 100% or less, more preferably, 80% or less and, further preferably, 50% or less.

[0252]

The shape of the organic silver salt can be measured by determining dispersion of an organic silver salt as transmission type electron microscopic images. Another method of measuring the mono-dispersion is a method of determining of the standard deviation of the volume weighted mean diameter of the organic silver salt in which the percentage for the value defined by the volume weight mean diameter (variation coefficient), is preferably, 100% or less, more preferably, 80% or less and, further preferably, 50% or less. For determination of such a value, a commercially available laser-beam scattering grain size analyzer can be used.

[0253]

The organic silver salt is prepared as shown below. The salt forming are carried out in an aqueous solvent and then the salt is dewatered, dried and then re-dispersed into a solvent such as MEK. Drying is preferably conducted in a airflow-type flash jet drier at a partial oxygen pressure of 15% by volume or less, more preferably, at 0.01% by volume to 15% by volume and, more preferably, at 0.01% by volume to 10% by volume.

[0254]

While an organic silver salt in the invention can be used in a desired amount, an amount of an organic silver salt is preferably in the range of from 0.1

g/m^2 to 5 g/m^2 in terms of coating amount of Ag and more preferably in the range of from 1 g/m^2 to 3 g/m^2 in terms of coating amount of Ag.

[0255]

5. Binder

As one embodiment of the photothermographic material of the invention, it is characterized that the binder has a glass transition temperature (Tg) of 45°C or higher. It is preferable that the Tg of a binder of the invention is in the range of from 50°C to 90°C, and further preferably from 50°C to 80°C.

The binder used in the invention can be selected from natural resin or synthetic resin; for example, included are gelatin, polyvinyl butyral, polyvinyl acetal, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefin, polyester, polystyrene, polyacrylonitrile, polycarbonate, butylethyl cellulose, methacrylate copolymer, maleic anhydride ester copolymers, polystyrene, and styrene-butadiene copolymers, and the like. In the image forming layer, in particularly, polyvinyl butyral is preferably incorporated as the binder. More specifically, polyvinyl butyral is added as a binder to account for 50 % by mass or more with respect to the total composition of the binder for the image forming layer.

[0256]

As a matter of fact, copolymers and terpolymers are also included. The preferable total amount of polyvinyl butyral is in a range of 50% by mass or more, more preferably, is in a range of 70% by mass or more with respect to total composition for the binder incorporated in the image forming layer.

[0257]

The total amount of the binders is such that, for instance, the component of the image forming layer can be sufficiently maintained within the layer. That is, the binders are used in an amount effective to function as binder. The effective range can be properly determined by those skilled in the art. In the case of holding at least an organic silver salt, the suitable ratio of binders to an orgagnic silver salts is from 15:1 to 1:3, particularly preferably, from 8:1 to 1:2 by weight.

[0258]

6. Development accelerator

In the photothermographic material of the invention a development accelerator can be added. Sulfoneamide phenolic compounds represented by the general formula (A) described in the specification of JP-A No. 2000-267222, and specification of JP-A No. 2000-330234, hindered phenolic compound represented by the general formula (II) described in JP-A No. 2001-92075, hydrazine series compounds represented by general formula (I) described in the specification of JP-A No. 10-62895 and the specification of JP-A No. 11-15116, represented by general formula (D) of JP-A No. 2002-156727 and represented by general formula (1) described in the specification of Japanese Patent Application No. 2001-074278, and phenolic or naphthalic compounds represented by general formula (2) described in the specification of JP-A No. 2001-264929 are used preferably as the development accelerator and they are added preferably. The development accelerator described above is used within a range from 0.1 mol% to 20 mol%, preferably, within a range from 0.5 mol% to 10 mol% and, more preferably, within

a range from 1 mol% to 5 mol% to the reducing agent. The introduction method to the photothermographic material can include, the same method as those for the reducing agent and, it is particularly preferred to add as a solution solved in an organic solvent.

[0259]

In the present invention, it is more preferred to use, among the development accelerators described above, hydrazine compounds represented by general formula (D) described in the specification of JP-A No. 2002-156727, and phenolic or naphtholic compounds represented by general formula (2) described in the specification of JP-A No. 2001-264929.

[0260]

Particularly preferred development accelerators of the invention are compounds represented by the following formulae (A-1) and (A-2).

Formula (A-1)

$$Q_1\text{-NHNH-}Q_2$$

(in which Q_1 represents an aromatic group or heterocyclic group coupling at a carbon atom to -NHNH-Q_2 and Q_2 represents a carbamoyl group, acyl group, alkoxycarbonyl group, aryloxycarbonyl group, sulfonyl group or sulfamoyl group).

[0261]

In formula (A-1), the aromatic group or heterocyclic group represented by Q_1 is, preferably, 5 to 7 membered unsaturated rings. Preferred examples are benzene ring, pyridine ring, pyrazine ring, pyrimidine ring, pyridazine ring, 1,2,4-

triazine ring, 1,3,5-triazine ring, pyrrole ring, imidazole ring, pyrazole ring, 1,2,3-triazole ring, 1,2,4-triazole ring, tetrazole ring, 1,3,4-thiadiazole ring, 1,2,4-thiadiazole ring, 1,2,5-thiadiazole ring, 1,3,4-oxadiazole ring, 1,2,4-oxadiazole ring, 1,2,5-oxadiazole ring, thiazole ring, oxazole ring, isothiazole ring, isooxazole ring, and thiophene ring. Condensed rings in which the rings described above are condensed to each other are also preferred.

[0262]

The rings described above may have substituents and in a case where they have two or more substituent groups, the substituents may be identical or different from each other. Examples of the substituents can include halogen atom, alkyl group, aryl group, carboamide group, alkylsulfoneamide group, arylsulfonamide group, alkoxy group, aryloxy group, alkylthio group, arylthio group, carbamoyl group, sulfamoyl group, cyano group, alkylsulfonyl group, arylsulfonyl group, alkoxycarbonyl group, aryloxycarbonyl group and acyl group. In a case where the substituents are groups capable of substituting, they may have further substituents and examples of preferred substituents can include halogen atom, alkyl group, aryl group, carbonamide group, alkylsulfoneamide group, arylsulfoneamide group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acyl group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, cyano group, sulfamoyl group, alkylsulfonyl group, arylsulfonyl group and acyloxy group.

[0263]

The carbamoyl group represented by Q_2 is a carbamoyl group preferably

having 1 to 50 carbon atoms and, more preferably, of 6 to 40 carbon atoms, for example, not-substituted carbamoyl, methyl carbamoyl, N-ethylcarbamoyl, N-propylcarbamoyl, N-sec-butylcarbamoyl, N-octylcarbamoyl, N-cyclohexylcarbamoyl, N-tert-butylcarbamoyl, N-dodecylcarbamoyl, N-(3-dodecyloxypropyl)carbamoyl, N-octadecylcarbamoyl, N-{3-(2,4-tert-pentylphenoxy)propyl} carbamoyl, N-(2-hexyldecyl)carbamoyl, N-phenylcarbamoyl, N-(4-dodecyloxyphenyl)carbamoyl, N-(2-chloro-5-dodecyloxycarbonylphenyl)carbamoyl, N-naphthylcarbaoyl, N-3-pyridylcarbamoyl and N-benzylcarbamoyl.

[0264]

The acyl group represented by Q_2 is an acyl group, preferably, having 1 to 50 carbon atoms and, more preferably, 6 to 40 carbon atoms and can include, for example, formyl, acetyl, 2-methylpropanoyl, cyclohexylcarbonyl, octanoyl, 2-hexyldecanoyl, dodecanoyl, chloroacetyl, trifluoroacetyl, benzoyl, 4-dodecyloxybenzoyl, and 2-hydroxymethylbenzoyl. Alkoxycarbonyl group represented by Q_2 is an alkoxycarbonyl group, preferably, of 2 to 50 carbon atoms and, more preferably, of 6 to 40 carbon atoms and can include, for example, methoxycarbonyl, ethoxycarbonyl, isobutyloxycarbonyl, cyclehexyloxycarbonyl, dodecyloxycarbonyl and benzyloxycarbonyl.

[0265]

The aryloxy carbonyl group represented by Q_2 is an aryloxycarbonyl group, preferably, having 7 to 50 carbon atoms and, more preferably, of 7 to 40 carbon atoms and can include, for example, phenoxycarbonyl, 4-octyloxyphenoxycarbonyl,

2-hydroxymethylphenoxycarbonyl, and 4-dodecyloxyphenoxycarbonyl. The sulfonyl group represented by Q_2 is a sulfonyl group, preferably, of 1 to 50 carbon atoms and, more preferably, of 6 to 40 carbon atoms and can include, for example, methylsulfonyl, butylsulfonyl, octylsulfonyl, 2-hexadecylsulfonyl, 3-dodecyloxypropylsulfonyl, 2-octyloxy-5-tert-octylphenyl sulfonyl, and 4-dodecyloxyphenyl sulfonyl.

[0266]

The sulfamoyl group represented by Q_2 is sulfamoyl group, preferably, having 0 to 50 carbon atoms, more preferably, 6 to 40 carbon atoms and can include, for example, not-substituted sulfamoyl, N-ethylsulfamoyl group, N-(2-ethylhexyl)sulfamoyl, N-decylsulfamoyl, N-hexadecylsulfamoyl, N-{3-(2-ethylhexyloxy)propyl}sulfamoyl, N-(2-chloro-5-dodecyloxycarbonylphenyl)sulfamoyl, and N-(2-tetradecyloxyphenyl)sulfamoyl. The group represented by Q_2 may further have a group mentioned as the example of the substituent of 5 to 7-membered unsaturated ring represented by Q_1 at the position capable of substituting. In a case where the group has two or more substituents, such substituents may be identical or different from each other.

[0267]

Then, preferred range for the compounds represented by formula (A-1) is to be described. 5 to 6 membered unsaturated ring is preferred for Q_1, and benzene ring, pyrimidine ring, 1,2,3-triazole ring, 1,2,4-triazole ring, tetrazole ring, 1,3,4-thiadiazole ring, 1,2,4-thiadiazole ring, 1,3,4-oxadiazole ring, 1,2,4-oxadiazole ring, thioazole ring, oxazole ring, isothiazole ring, isooxazole ring and

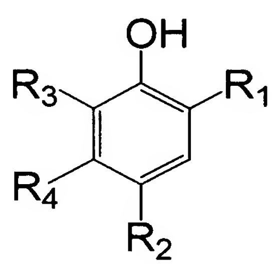
a ring in which the ring described above is condensed with a benzene ring or unsaturated hetero ring are further preferred. Further, Q_2 is preferably a carbamoyl group and, particularly, a carbamoyl group having hydrogen atom on the nitrogen atom is particularly preferred.

[0268]

Formula (A-2)

[0269]

[F28]



[0270]

In formula (A-2), R_1 represents an alkyl group, acyl group, acylamino group, sulfoneamide group, alkoxycarbonyl group, and carbamoyl group. R_2 represents a hydrogen atom, halogen atom, alkyl group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acyloxy group and carbonate ester group. R_3, R_4 each represents a group capable of substituting for a hydrogen atom on a benzene ring which is mentioned as the example of the substituent for formula (A-1). R_3 and R_4 may join to each other to form a condensed ring.

[0271]

R_1 is, preferably, an alkyl group having 1 to 20 carbon atoms (for example,

methyl group, ethyl group, isopropyl group, butyl group, tert-octyl group, or cyclohexyl group), acylamino group (for example, acetylamino group, benzoylamino group, methylureido group, or 4-cyanophenylureido group), carbamoyl group (for example, n-butylcarbamoyl group, N,N-diethylcarbamoyl group, phenylcarbamoyl group, 2-chlorophenylcarbamoyl group, or 2,4-dichlorophenylcarbamoyl group), acylamino group (including ureido group or urethane group) being more preferred. R_2 is, preferably, a halogen atom (more preferably, chlorine atom, bromine atom), alkoxy group (for example, methoxy group, butoxy group, n-hexyloxy group, n-decyloxy group, cyclohexyloxy group or benzyloxy group), and aryloxy group (phenoxy group or naphthoxy group).

[0272]

R_3 is, preferably a hydrogen atom, halogen atom or an alkyl group having 1 to 20 carbon atoms, the halogen atom being most preferred. R_4 is preferably a hydrogen atom, alkyl group or an acylamino group, with the alkyl group or the acylamino group being more preferred. Examples of the preferred substituent thereof are identical with those for R_1. In a case where R_4 is an acylamino group, R_4 may preferably be joined with R_3 to form a carbostyryl ring.

[0273]

In a case where R_3 and R_4 in formula (A-2) are joined to each other to form a condensed ring, a naphthalene ring is particularly preferred as the condensed ring. The same substituent as the example of the substituent referred to for formula (A-1) may be joined to the naphthalene ring. In a case where formula (A-2) is a naphtholic compound, R_1, is, preferably, a carbamoyl group. Among them,

benzoyl group is particularly preferred. R_2 is, preferably, an alkoxy group or aryloxy group and, particularly, preferably an alkoxy group.

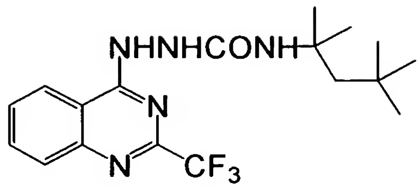
[0274]

Preferred specific examples for the development accelerator of the invention are to be described below. The invention is not restricted to them.

[0275]

[F29]

(A-1)



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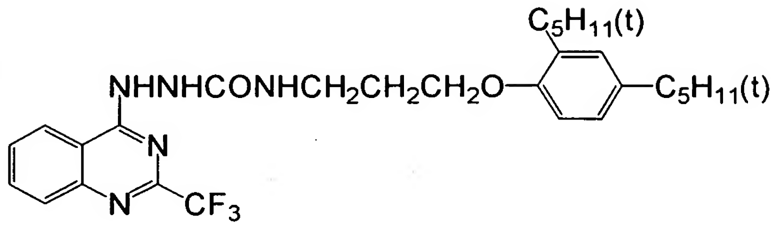
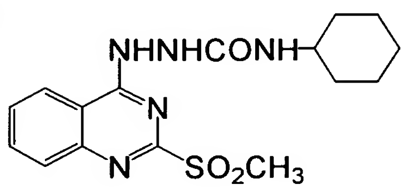
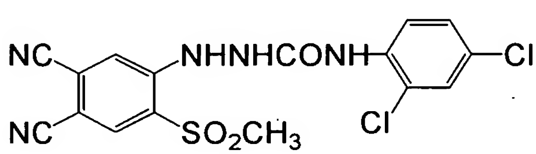


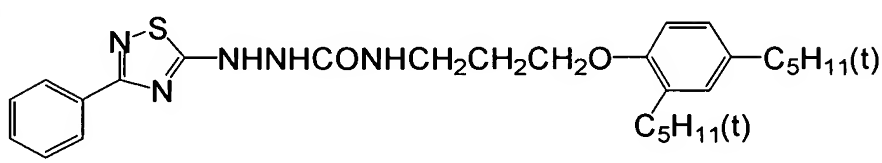
(A-3)



(A-4)



(A-5)



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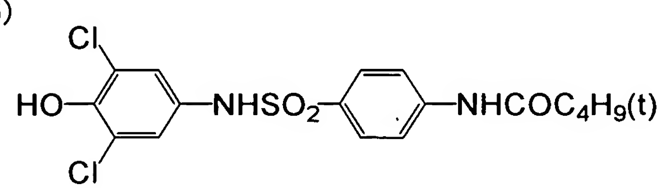

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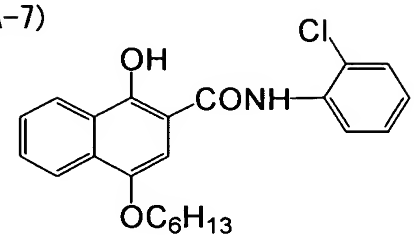

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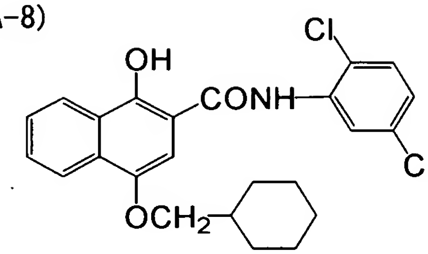

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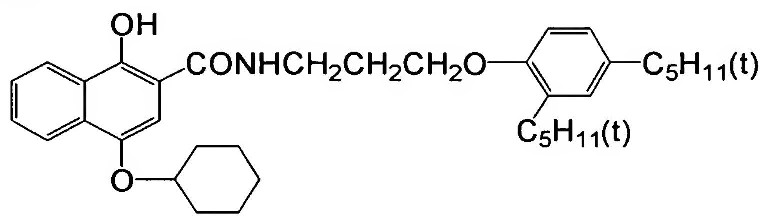
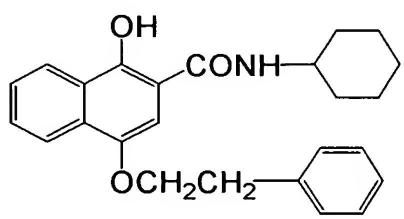
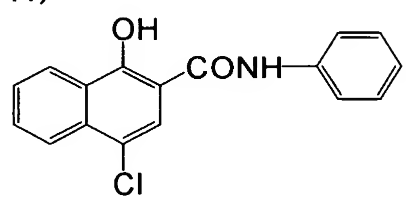


(A-10)



(A-11)



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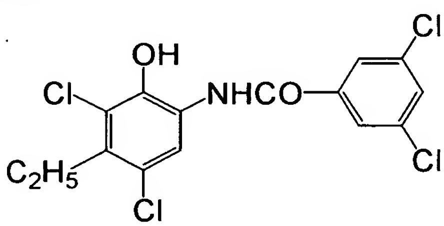


[0276]

7. Hydrogen bonding compound

In the invention, in the case that the reducing agent has an aromatic hydroxyl group (-OH) or an amino group, particularly in the case that the reducing agent is a bisphenol described above, it is preferred to use in combination, a non-

reducing compound having a group capable of reacting with these groups of the reducing agent, and that is also capable of forming a hydrogen bond therewith.

[0277]

As a group forming a hydrogen bond with a hydroxyl group or an amino group, there can be mentioned a phosphoryl group, a sulfoxido group, a sulfonyl group, a carbonyl group, an amido group, an ester group, an urethane group, an ureido group, a tertiary amino group, a nitrogen-containing aromatic group, and the like. Particularly preferred among them is phosphoryl group, sulfoxido group, amido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), urethane group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), and ureido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)).

[0278]

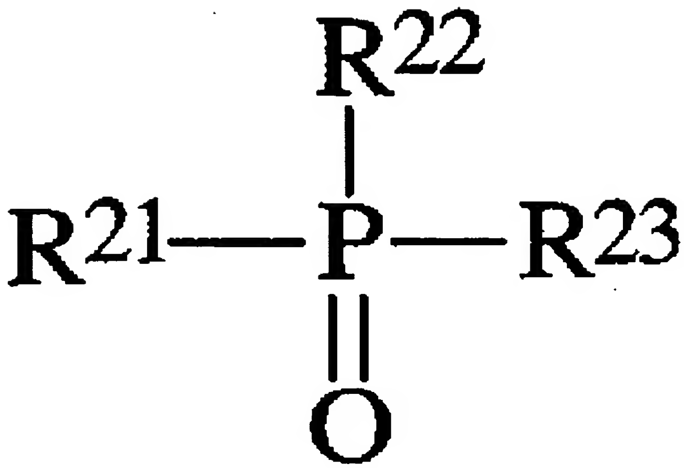
In the invention, particularly preferable as the hydrogen bonding compound is the compound expressed by formula (D) shown below.

[0279]

Formula (D)

[0280]

[F30]



[0281]

In formula (D), R^{21} to R^{23} each independently represent an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, or a heterocyclic group, which may be substituted or not substituted.

[0282]

In the case R^{21} to R^{23} contain a substituent, examples of the substituents include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamido group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a phosphoryl group, and the like, in which preferred as the substituents are an alkyl group or an aryl group, e.g., methyl group, ethyl group, isopropyl group, t-butyl group, t-octyl group, phenyl group, a 4-alkoxyphenyl group, a 4-acyloxyphenyl group, and the like.

[0283]

Specific examples of an alkyl group expressed by R^{21} to R^{23} include methyl group, ethyl group, butyl group, octyl group, dodecyl group, isopropyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, phenetyl group, 2-phenoxypropyl group, and the like.

[0284]

As aryl groups, there can be mentioned phenyl group, cresyl group, xylyl group, naphthyl group, 4-t-butylphenyl group, 4-t-octylphenyl group, 4-anisidyl group, 3,5-dichlorophenyl group, and the like.

[0285]

As alkoxyl groups, there can be mentioned methoxy group, ethoxy group, butoxy group, octyloxy group, 2-ethylhexyloxy group, 3,5,5-trimethylhexyloxy group, dodecyloxy group, cyclohexyloxy group, 4-methylcyclohexyloxy group, benzyloxy group, and the like.

[0286]

As aryloxy groups, there can be mentioned phenoxy group, cresyloxy group, isopropylphenoxy group, 4-t-butylphenoxy group, naphthoxy group, biphenyloxy group, and the like.

[0287]

As amino groups, there can be mentioned are dimethylamino group,

diethylamino group, dibutylamino group, dioctylamino group, N-methyl-N-hexylamino group, dicyclohexylamino group, diphenylamino group, N-methyl-N-phenylamino, and the like.

[0288]

Preferred as R^{21} to R^{23} are an alkyl group, an aryl group, an alkoxy group, and an aryloxy group. Concerning the effect of the invention, it is preferred that at least one or more of R^{21} to R^{23} are an alkyl group or an aryl group, and more preferably, two or more of them are an alkyl group or an aryl group. From the viewpoint of low cost availability, it is preferred that R^{21} to R^{23} are of the same group.

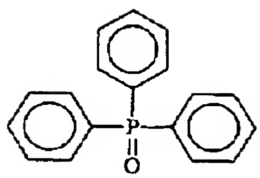
[0289]

Specific examples of hydrogen bonding compounds represented by formula (D) of the invention and others are shown below, but it should be understood that the invention is not limited thereto.

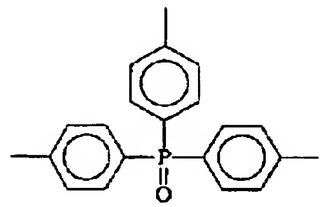
[0290]

[F31]

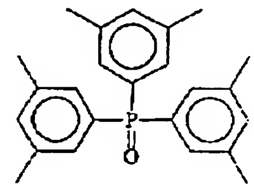
(D－1)



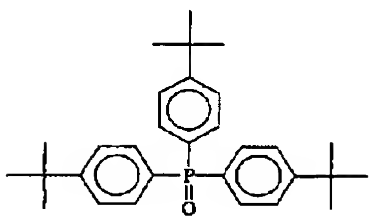
(D－2)



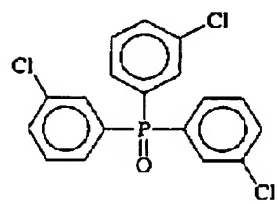
(D－3)



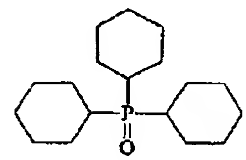
(D－4)



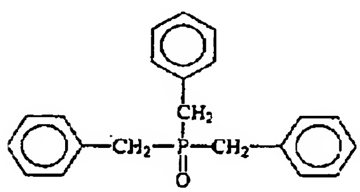
(D－5)



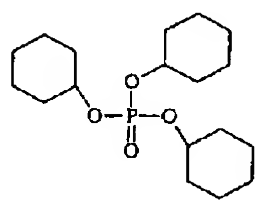
(D－6)



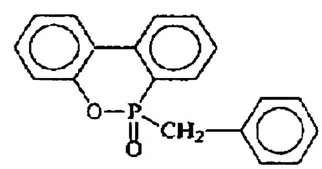
(D－7)



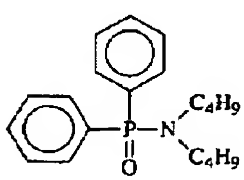
(D－8)



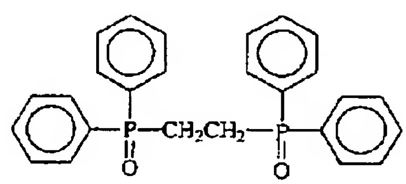
(D－9)



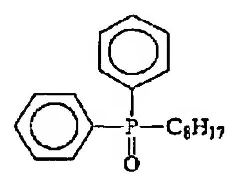
(D－10)



(D－11)



(D－12)



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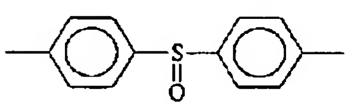

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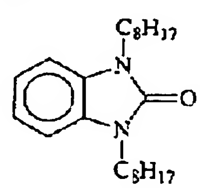

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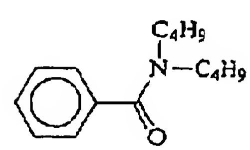


[0291]

Specific examples of hydrogen bonding compounds other than those enumerated above can be found in those described in European Patent No. 1096310, JP-A No. 2002-156727 and Japanese Patent Application No. 2001-124796.

[0292]

The compound expressed by formula (D) in the invention can be used in the photothermographic material by being incorporated into the coating solution in the form of solution, emulsion dispersion, or similar to the case of reducing agent. In the solution, these compounds forms a hydrogen-bonded complex with a compound having a phenolic hydroxyl group, and can be isolated as a complex in crystalline state depending on the combination of the reducing agent and the compound expressed by formula (D).

[0293]

The compound expressed by formula (D) in the invention is preferably used in a range of from 1 mol% to 200 mol%, more preferably from 10 mol% to 150 mol%, and most preferably, from 20 mol% to 100 mol%, with respect to the reducing agent.

[0294]

8. Other additives

1) Disulfide compounds

In the invention, mercapto compounds, disulfide compounds, and thione compounds may be added in order to control the development by suppressing or

enhancing development, to improve spectral sensitization efficiency, or to improve storage properties before and after development. It is preferred to include the compound expressed by Ar-SM or Ar-S-S-Ar. In the formula, M represents a hydrogen atom or an alkali metal atom; Ar represents an aromatic ring, or a condensed aromatic ring, having one or more nitrogen, sulfur, oxygen, selenium, or tellurium atom.

[0295]

For example, preferable is benzimidazole, naphthoimidazole, benzthiazole, naphthothiazole, benzoxazole, naphthoxazole, benzselenazole, benztellurazole, imidazole, oxazole, pyrrazole, triazole, thiadiazole, tetrazole, triazine, pyrimidine, pyridazine, pyrazine, pyridine, purine, quinoline, or quinazolinone. Benzimidazole, benzthiazole or benztellurazole is more preferable.

[0296]

These aromatic ring may have a substituent selected from, for example, a halogen (e.g., Br and Cl), a hydroxyl group, an amino group, a carboxy group, an alkyl group (e.g., preferably, such having 1 to 4 carbon atoms), an alkoxy group (e.g., preferably, such having 1 to 4 carbon atoms), and an aryl group (which may have a sustituent).

[0297]

The addition amount of disulfide compounds is preferably in a range of from 0.001 mol to 1.0 mol, and more preferably, 0.003 mol to 0.1 mol, per one mol of silver in the image forming layer.

[0298]

2) Toner

In the photothermographic material of the present invention, the addition of a toner is preferred. The description of the toner can be found in JP-A No.10-62899 (paragraph Nos. 0054 to 0055), EP-A No.0803764A1 (page21, lines 23 to 48), JP-A Nos.2000-356317 and 2000-187298. Preferred are phthalazinones (phthalazinone, phthalazinone derivatives and metal salts thereof, e.g.,4-(1-naphthyl)phthalazinone,6-chlorophthalazinone, 5,7-dimethoxyphthalazinone and 2,3-dihydro-1,4-phthalazinedione); combinations of phthalazinones and phthalic acids(e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, diammonium phthalate, sodium phthalate, potassium phthalate and tetrachlorophthalic anhydride); phthalazines(phthalazine, phthalazine derivatives and metal salts thereof, e.g., 4-(1-naphthyl)phthalazine, 6-isopropylphthalazine, 6-ter-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine); combinations of phthalazines and phthalic acids. In the case used together with the silver halide having a high silver iodide content, particularly preferred is a combination of phthalazines and phthalic acids.

[0299]

The addition amount of toner is preferably in a range of from 0.1 mol% to 50 mol%, and more preferably 0.5 mol% to 20 mol%, per one mol of silver in the image forming layer.

[0300]

3) Antifoggant

In the invention, the compounds represented by formula (H) described below are preferably used as the antifoggant.

[0301]

Formula (H)

$$Q\text{-}(Y)n\text{-}C(Z_1)(Z_2)X$$

[0302]

In formula (H), Q represents an alkyl group, an aryl group, or a heterocyclic group; Y represents a divalent connecting group; n represents 0 or 1; Z_1 and Z_2 each respectively represent a halogen atom; and X represents hydrogen atom or an electron attracting group.

[0303]

In formula (H), Q preferably is a phenyl group substituted by an electron-attracting group whose Hammett substitution coefficient σp yields a positive value. For the details of Hammett substitution coefficient, reference can be made to Journal of Medicinal Chemistry, Vol. 16, No. 11 (1973), pp. 1207 to 1216, and the like.

[0304]

As such electron-attracting groups, examples include, halogen atoms (fluorine atom (σp value: 0.06), chlorine atom (σp value: 0.23), bromine atom (σp value: 0.23), iodine atom (σp value: 0.18)), trihalomethyl groups (tribromomethyl

(σp value: 0.29), trichloromethyl (σp value: 0.33), trifluoromethyl (σp value: 0.54)), a cyano group (σp value: 0.66), a nitro group (σp value: 0.78), an aliphatic aryl or heterocyclic sulfonyl group (for example, methanesulfonyl (σp value: 0.72)), an aliphatic aryl or heterocyclic acyl group (for example, acetyl (σp value: 0.50) and benzoyl (σp value: 0.43)), an alkinyl (e.g., C≡CH (σp value: 0.23)), an aliphatic aryl or heterocyclic oxycarbonyl group (e.g., methoxycarbonyl (σp value: 0.45) and phenoxycarbonyl (σp value: 0.44)), a carbamoyl group (σp value: 0.36), sulfamoyl group (σp value: 0.57), sulfoxido group, heterocyclic group, and phosphoryl group.

Preferred range of the σp value is from 0.2 to 2.0, and more preferably, from 0.4 to 1.0.

[0305]

Preferred as the electron-attracting groups are a carbamoyl group, an alkoxycarbonyl group, an alkylsulfonyl group, an alkylphosphoryl group, a carboxyl group, an alkylcarbonyl group, and an arylcarbonyl group, particularly preferred among them are a carbamoyl group, an alkoxycarbonyl group, an alkylsulfonyl group, an alkylphosphoryl group, and most preferred among them is a carbamoyl group.

[0306]

X preferably is an electron-attracting group, more preferably, a halogen atom, an aliphatic aryl or heterocyclic sulfonyl group, an aliphatic aryl or heterocyclic acyl group, an aliphatic aryl or heterocyclic oxycarbonyl group, carbamoyl group, or sulfamoyl group; particularly preferred among them is a

halogen atom.

[0307]

Among halogen atoms, preferred are chlorine atom, bromine atom, and iodine atom; more preferred are chlorine atom and bromine atom; and particularly preferred is bromine atom.

Y preferably represents –C(=O)-, -SO-, or $-SO_2$-; more preferably, –C(=O)- or $-SO_2$-; and particularly preferred is $-SO_2$-. n represents 0 or 1, and preferred is 1.

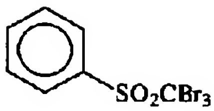
[0308]

Specific examples of the compounds expressed by formula (H) of the invention are shown below.

[0309]

[F32]

(4-1)



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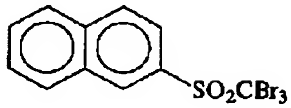

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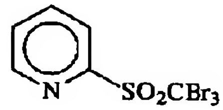

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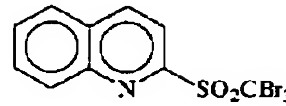

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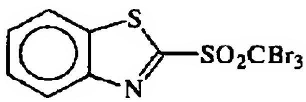

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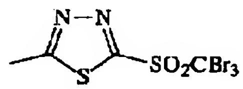

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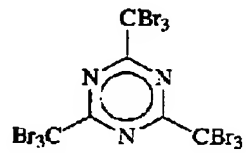

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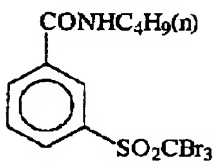

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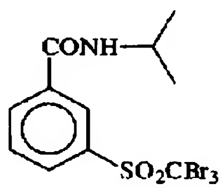

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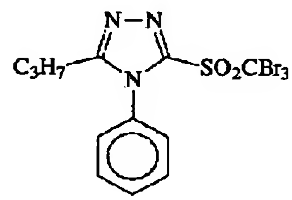

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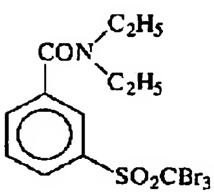

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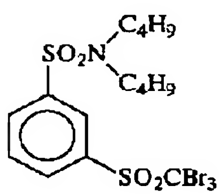

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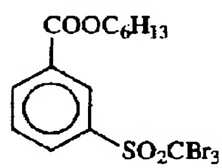
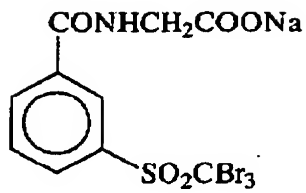


[0310]

[F33]

(4－14)



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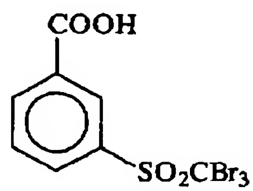

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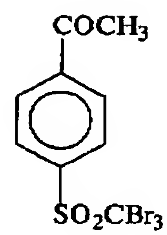

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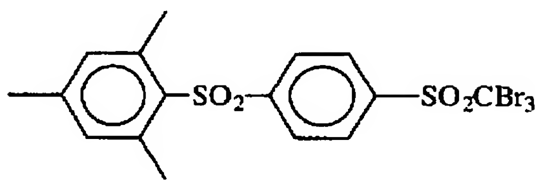

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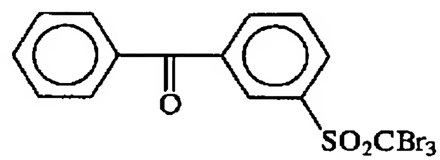

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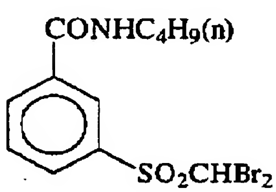

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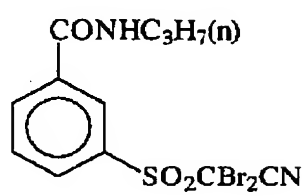

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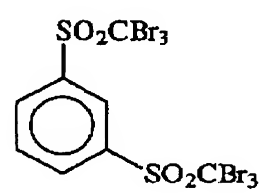

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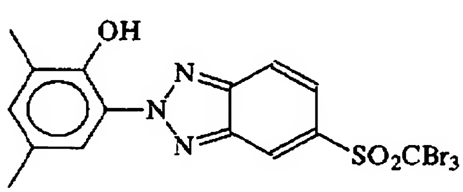

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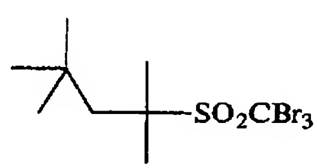


[0311]

A compound expressed by the formula (H) in the invention is preferably used in the range of from 10^{-4} mol to 0.8 mol per one mole of a non-photosensitive

silver salt in an image forming layer, more preferably used in the range of from 10^{-3} mol to 0.1 mol and still more preferably used in the range of from 5×10^{-3} mol to 0.05 mol.

[0312]

Particularly, in a case where a silver halide having a composition of a high silver iodide content, an amount of addition of a compound expressed by formula (H) is important in order to obtain a sufficient anti-fogging effect and the compound is most preferably used in the range of from 5×10^{-3} mol to 0.03 mol.

[0313]

In the invention, a method of incorporating a compound expressed by formula (H) into a photosensitive material is described in a method of incorporating a reducing agent described above.

[0314]

A melting point of a compound expressed by formula (H) is preferably 200°C or lower and more preferably 170°C or lower.

[0315]

Examples of other organic polyhalogen compounds used in the invention are disclosed in paragraphs Nos. 0111 to 0112 of JP-A No. 11-65021. Preferable examples thereof are an organic polyhalogen compound expressed by the formula (P) described in JP-A No. 11-87297, an organic polyhalogen compound expressed by general formula (II) described in JP-A No. 10-339934 and an organic

polyhalogen compound described in Japanese Patent Application No. 11-205330.

[0316]

4) Other antifoggants

Examples of antifoggants and stabilizers or precursors thereof suitable for independent use or combined use include the thiazolium salts disclosed in USP Nos. 2131038 and 2694716, the azaindenes disclosed in USP Nos. 2886487 and 2444605, the compounds disclosed in JP-A No.9-329865 and USP No. 6083681, the mercury salts disclosed in USP No. 2728663, the urazoles disclosed in USP No.3287135, the sulfocatechols disclosed in USP No.3235652, the oximes, the nitrones and nitroindazoles disclosed in GBP No.623448, the polyvalent metal salts disclosed in USP No. 2839405, the thiuronium salts disclosed in USP No. 3220839, the palladium, platinum and gold salts disclosed in USP Nos. 2566263 and 2597915, the halogen-substituted organic compounds disclosed in USP Nos. 4108665 and 4442202, the triazines disclosed in USP Nos. 4128557, 4137079, 4138365 and 4459350, and the phosphorus compounds disclosed in USP No. 4411985.

[0317]

In some cases, it is advantageous that the present photothermographic material contains in its photosensitive layer a mercury(II) salt as an antifoggant. The mercury(II) salts appropriate for this purpose are mercury(II) acetate and mercury(II) bromide. The suitable amount of mercury used in the invention is in the range of 1 nanomole to 1 millimole, preferably 10 nanomoles to 100 micromoles, per one mole of coated silver.

[0318]

The present photothermographic material may contain benzoic acids for the purposes of sensitivity increase and fog prevention. The benzoic acids used for these purposes may include any of benzoic acid derivatives. Examples of a benzoic acid derivative having a favorable structure include the compounds disclosed in USP Nos. 4784939 and 4152160, and JP-A Nos.9-281687, 9-329864 and 9-329865. The benzoic acids used in the invention may be added to any part of the photothermographic material, but it is preferable to add them to a layer arranged on the photosensitive layer side, particularly to the layer containing organic silver salt. As to the addition time of benzoic acids, the acids may be added at any stage in the process of preparing a coating solution. In the case of adding benzoic acids to the organic silver salt-containing layer, the benzoic acids may be added at any stage during a period from the preparation of the organic silver salts to the preparation of the coating solution. However, it is preferable that the benzoic acids be added during the period from the conclusion of the preparation of organic silver salts to just before the coating operation. The benzoic acids may be added according to any method. For instance, a method of adding them in the form of a powder, a solution or a dispersion of fine particles can be adopted. On the other hand, a mixture may be prepared from the benzoic acids and other additives, such as a sensitizing dye, a reducing agent and a toner, and added as a solution thereof. In the invention, the benzoic acids may be added in any amount, but it is appropriate to add them in an amount of 1 micromole to 2 moles, preferably 1 millimole to 0.5 mole, per one mole of silver.

[0319]

The present photothermographic material may contain azolium salts for the purpose of fog prevention. Examples of an azolium salt usable for such a purpose include the compounds represented by formula (XI) in JP-A No.59-193447, the compounds disclosed in JP-B No.55-12581, and the compounds represented by formula (II) in JP-A No.60-153039. Although the azolium salts may be added to any part of the photothermographic material, it is preferable to add them to a layer arranged on the photosensitive layer side, especially to the layer containing organic silver salts.

[0320]

As to the addition time of azolium salts, the salts may be added at any stage in the process of preparing a coating solution. In the case of adding azolium salts to the organic silver salt-containing layer, the azolium salts may be added at any stage during a period from the preparation of the organic silver salts to the preparation of the coating solution. However, it is preferable that the azolium salts be added during the period from the conclusion of the preparation of organic silver salts to just before the coating operation. The azolium salts may be added according to any method. For instance, a method of adding them in the form of a powder, a solution or a dispersion of fine particles can be adopted. On the other hand, a mixture may be prepared from the azolium salts and other additives, such as a sensitizing dye, a reducing agent and a toner, and added as a solution thereof.

[0321]

In the invention, the azolium salts may be added in any amount, but it is appropriate to add them in an amount of 1×10^{-6} mole to 2 moles, preferably 1×10^{-3} mole to 0.5 mole, per one mole of silver.

[0322]

5) Plasticizer and lubricant

Plasticizers and lubricants usable in the photothermographic material of the invention are described in paragraph No. 0117 of JP-A No. 11-65021. Lubricants are described in paragraph Nos. 0061 to 0064 of JP-A No. 11-84573 and in paragraph Nos. 0049 to 0062 of Japanese Patent Application No. 11-106881.

[0323]

6) Dyes and pigments

From the viewpoint of improving image tone, of preventing the generation of interference fringes and of preventing irradiation on laser exposure, various types of dyes and pigments may be used in the photosensitive layer of the invention.

[0324]

The image forming layer of the invention preferably has an absorption of 0.1 to 0.6, and more preferably, 0.2 to 0.5, at the exposing wavelength. In the case absorption is large, Dmin increases to make images difficult to discriminate, and in the case absorption is low, sharpness becomes impaired. Any methods may be employed to impart absorption to the photosensitive layer of the invention, but it is preferred to use a dye. Usable as the dyes are any of those satisfying the

absorption conditions above; for instance, there can be mentioned pyrazoloazole dyes, anthraquinone dyes, azo dyes, azomethine dyes, oxonol dyes, carbocyanine dyes, styryl dyes, triphenylmethane dyes, indoaniline dyes, indophenol dyes, squalilium dyes, and the like. As preferred dyes for use in the invention, there can be mentioned an anthraquinone dye (e.g., compounds 1 to 9 described in JP-A No. 5-341441, compounds 3-6 to 3-18 and 3-23 to 3-38 described in JP-A No. 5-165147, and the like), an azomethine dye (e.g., compounds 17 to 47 described in JP-A No. 5-341441), an indoaniline dye (e.g., compounds 11 to 19 described in JP-A No. 5-289227, compound 47 described in JP-A No. 5-341441, compounds 2-10 to 2-11 described in JP-A No. 5-165147), an azo dye (e.g., compounds 10 to 16 described in JP-A No. 5-341441), and squalilium dye (e.g., compounds 1 to 20 described in JP-A No. 10-104779, and compounds 1a to 3d disclosed in USP No. 5,380,635). These dyes can be added by any means, for instance, in the form of solution, emulsion, solid-dispersed fine particle dispersion, or mordanted by polymer mordant, and the like. The addition amount of these dyes or pigments is determined depending on the targeted absorption; in general, it is preferably used in an amount of 1 μg to 1 g per 1 m^2.

[0325]

Further, the light-absorbing substances as disclosed in USP Nos. 3253921, 2274782, 2527583 and 2956879 can be included as filter dyes in a surface protective layer. In addition, the dyes can be mordanted as described in USP No. 3282699. It is appropriate that the filter dyes be used in an amount to provide an absorbance of 0.1 to 3, particularly preferably 0.2 to 1.5, at the exposure wavelengths.

[0326]

In the present photothermographic material, it is appropriate that the light absorption by any part other than the layer containing photosensitive silver halide grains be from 0.1 to 3.0 at the exposure wavelengths, preferably from 0.3 to 2.0 in respect of anti-halation. The part having absorption at the exposure wavelengths is preferably a layer arranged on the side of the support opposing to the layer containing photosensitive silver halide grains (e.g., a back layer, an undercoating or subbing layer on the back of the support, a protective layer for a back layer), or a layer between the support and the layer containing photosensitive silver halide grains (e.g., an undercoating or subbing layer).

[0327]

Additionally, the present photosensitive silver halide grains are spectrally sensitized in the infrared region. In causing the part other than the layer containing photosensitive silver halide grains to have absorption, any method may be adopted. Therein, however, it is preferable to control the absorption maximum in the visible region to 0.3 or below. The dyes used therefor can be dyes similar to those used for causing the photosensitive silver halide layer to have absorption, or they may be the same as or different from the dyes used in the photosensitive silver halide layer.

[0328]

7) Ultra-high contrast promoting agent

In order to form ultra-high contrast image suitable for use in graphic arts,

it is preferred to add an ultra-high contrast promoting agent into the image forming layer. Details on the ultra-high contrast promoting agents, method of their addition and addition amount can be found in paragraph No. 0118 of JP-A No. 11-65021, paragraph Nos. 0136 to 0193 of JP-A No. 11-223898, as compounds expressed by formulae (H), (1) to (3), (A), and (B) in Japanese Patent Application No. 11-87297, as compounds expressed by formulae (III) to (V)(specific compound: chemical No.21 to chemical No.24) in Japanese Patent Application No. 11-91652; as an ultra-high contrast accelerator, description can be found in paragraph No. 0102 of JP-A No. 11-65021, and in paragraph Nos. 0194 to 0195 of JP-A No. 11-223898.

[0329]

In the case of using formic acid or formates as a strong fogging agent, it is preferably incorporated into the side having thereon the image forming layer containing photosensitive silver halide, at an amount of 5 mmol or less, preferably, one mmol or less per one mol of silver.

[0330]

In the case of using an ultra-high contrast promoting agent in the photothermographic material of the invention, it is preferred to use an acid resulting from hydration of diphosphorus pentaoxide, or its salt in combination. Acids resulting from the hydration of diphosphorus pentaoxide or salts thereof include metaphosphoric acid (salt), pyrophosphoric acid (salt), orthophosphoric acid (salt), triphosphoric acid (salt), tetraphosphoric acid (salt), hexametaphosphoric acid (salt), and the like. Particularly preferred acids

obtainable by the hydration of diphosphorus pentaoxide or salts thereof include orthophosphoric acid (salt) and hexametaphosphoric acid (salt). Specifically mentioned as the salts are sodium orthophosphate, sodium dihydrogen orthophosphate, sodium hexametaphosphate, ammonium hexametaphosphate, and the like.

[0331]

The addition amount of the acid obtained by hydration of diphoshorus pentaoxide or the salt thereof (i.e., the coverage per 1 m^2 of the photosensitive material) may be set as desired depending on the sensitivity and fogging, but preferred is an amount of 0.1 mg/m^2 to 500 mg/m^2, and more preferably, of 0.5 mg/m^2 to 100 mg/m^2.

[0332]

9. Layer structure, and other components

The present photothermographic material can have non-photosensitive layers in addition to the image forming layer. The non-photosensitive layers can be classified by their locations under the following four groups: (a) surface protective layers provided on the image forming layer (on the side distant from the support), (b) intermediate layers provided between a plurality of image forming layers and between an image forming layer and the protective layer, (c) undercoating layers provided between an image forming layer and the support, and (d) back layers provided on the side opposing to the image forming layer.

[0333]

Further, a layer functioning as an optical filter can be provided, and it is classified as the layer belonging to the group (a) or (b). The antihalation layer is provided as the layer belonging to the group (c) or (d) in the photothermographic material.

[0334]

1) Surface protective layer

In the present photothermographic material, a surface protective layer can be provided for the purpose of preventing adhesion of the image forming layer. The surface protective layer may be a single layer or a multiple layer.

[0335]

The binder used in the surface protective layer may be any polymer. Examples of a polymer usable as the binder include polyester, gelatin, polyvinyl alcohol and cellulose derivatives. Among these polymers, cellulose derivatives are preferred over the others. Examples of cellulose derivatives are recited below, but cellulose derivatives usable in the invention should not be construed as being limited to these examples. Specifically, the cellulose derivatives include cellulose acetate, cellulose acetate butyrate, cellulose propionate, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, methyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose and mixtures thereof. The suitable thickness of the surface protective layer is from 0.1 μm to 10 μm, preferably from 1 μm to 5 μm.

[0336]

In the surface protective layer, any abherent may be used. Examples of

an abherent usable herein include wax, liquid paraffin, silica particles, styrene-containing elastomeric block copolymers (e.g., styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer), cellulose acetate, cellulose acetate butyrate, cellulose propionate, and mixtures thereof.

[0337]

2) Antihalation layer

Descriptions on the antihalation layer can be found in paragraph Nos. 0123 to 0124 of JP-A No. 11-65021, in JP-A Nos. 11-223898, 9-230531, 10-36695, 10-104779, 11-231457, 11-352625, 11-352626, and the like.

[0338]

The antihalation layer contains an antihalation dye having its absorption at the wavelength of the exposure light. In the case the exposure wavelength is in the infrared region, an infrared-absorbing dye may be used, and in such a case, preferred are dyes having no absorption in the visible region.

[0339]

In the case of preventing halation from occurring by using a dye having absorption in the visible region, it is preferred that the color of the dye would not substantially reside after image formation, and is preferred to employ a means for bleaching color by the heat of thermal development; in particular, it is preferred to add a thermal bleaching dye and a base precursor to the non-photosensitive layer to impart function as an antihalation layer. Those techniques are described in JP-A No. 11-231457 and the like.

[0340]

The amount of adding the thermal bleaching dye is determined depending on the usage of the dye. In general, it is used at an amount as such that the optical density (absorbance) exceeds 0.1 when measured at the desired wavelength. The optical density is preferably in a range of from 0.2 to 2. The usage of dyes to obtain optical density in the above range is generally from 0.001 g/m^2 to 1 g/m^2.

[0341]

By thermal bleaching the dye in such a manner, the optical density after thermal development can be lowered to 0.1 or lower. Two types or more of thermal bleaching dyes may be used in combination in a photothermographic material. Similarly, two types or more of base precursors may be used in combination.

[0342]

In the case of thermal decolorization by the combined use of a decoloring dye and a base precursor, it is advantageous from the viewpoint of thermal decolorization efficiency to further use the substance capable of lowering the melting point by at least 3°C when mixed with the base precursor (e.g., diphenylsulfone, 4-chlorophenyl(phenyl)sulfone) as disclosed in JP-A No. 11-352626.

[0343]

3) Back layer

Back layers usable in the invention are described in paragraph Nos. 0128 to 0130 of JP-A No. 11-65021.

[0344]

Any type of polymer may be used as the binder for the back layer. Suitable as the binder are those that are transparent or translucent, and that are generally colorless, such as natural resin or polymer and their copolymers; synthetic resin or polymer and their copolymer; or media forming a film; for example, included are gelatin, rubber, poly(vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly(vinyl pyrrolidone), casein, starch, poly(acrylic acid), poly(methylmethacrylic acid), poly(vinyl chloride), poly(methacrylic acid), styrene-maleic anhydride copolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(vinyl acetal)(e.g., poly(vinyl formal) and poly(vinyl butyral)), poly(ester), poly(urethane), phenoxy resin, poly(vinylidene chloride), poly(epoxide), poly(carbonate), poly(vinyl acetate), poly(olefin), cellulose esters, and poly(amide). A binder may be used with water, an organic solvent or emulsion to form a coating solution.

[0345]

In the invention, coloring matters having maximum absorption in the wavelength range of from 300 nm to 450 nm may be added in order to improve a color tone of developed images and a deterioration of the images during aging. Such coloring matters are described in, for example, JP-A Nos. 62-210458, 63-104046, 63-103235, 63-208846, 63-306436, 63-314535, and 01-61745, Japanese Patent Application No. 11-276751, and the like. Such coloring matters are

generally added in the range of from 0.1 mg/m^2 to 1 g/m^2, preferably to the back layer provided to the side opposite to the photosensitive layer.

[0346]

4) Matting agent

A matting agent may be preferably added to the surface protective layer or to the back layer in order to improve transportability.

[0347]

The matness on the image forming layer surface is not restricted as far as star-dust trouble occurs, but the matness of 200 seconds to 10000 seconds is preferred, particularly preferred, 300 seconds to 8000 seconds as Beck's smoothness. Beck's smoothness can be calculated easily, by seeing Japan Industrial Standared (JIS) P8119 "The method of testing Beck's smoothness for papers and sheets using Beck's test apparatus", or TAPPI standard method T479.

[0348]

The matt degree of the back layer in the invention is preferably in a range of 250 seconds or less and 10 seconds or more; more preferably, 180 seconds or less and 50 seconds or more; most preferably, 500 seconds or less and 40 seconds or more when expressed by Beck smoothness.

[0349]

In the invention, the matting agent is incorporated preferably in the outermost surface layer of the photothermographic material or a layer functioning

as the outermost surface layer, or a layer near to the outer surface, and a layer that functions as the so-called protective layer.

[0350]

The matting agent in the present invention is generally an organic or an inorganic fine particle insoluble to the coating solution. For example, the organic matting agent described in U.S. Patent Nos. 1939213, 2701245, 2322037, 3262782, 3539344 and 3767448, and the like, the inorganic matting agent described in the specifications of U.S. Patent Nos. 1260772, 2192241, 3257206, 3370951, 3523022 and 3769020, and the like. These are well known in the said industry. As the organic compound usable as a matting agent, aqueous dispersed vinyl polymers such as polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, acrylonitrile/α-methylstyrene copolymer, polystyrene, styrene/divinylbenzene copolymer, polyvinyl acetate, polyethylene carbonate, polytetrafluoroethylene and the like, cellulose derivatives such as methylcellulose, cellulose acetate, cellulose acetate propionate and the like, starch derivatives such as carboxy starch, carboxynitrophenyl starch, reaction product of urea – formaldehyde – starch and the like, hardened gelatin by known hardener and the like, hardened gelatin as a fine hollow capsule particle by a coacervated hardening are preferably used. As examples of inorganic compound, silicon dioxide, titanium dioxide, magnesium dioxide, aluminium oxide, barium sulfate, calcium carbonate, silver chloride and silver bromide desensitized by known method, glass, diatomaceous earth and the like are preferably used. The different kind of compound can be used by mixing with the above matting agent if necessary. There is no limitation according to the size and form of matting agent, an arbitrary particle size can be used. In this

invention, particle size of matting agent is preferably 0.1 μm to 30 μm. And the size distribution can be any of narrow and wide. On the other side, as a matting agent effects greatly to haze and surface gloss, it is preferred that the particle size, the shape and the size distribution are arranged in the suitable condition in proportion to the need at the making time of the matting agent or at the mixing time of the plural matting agents.

[0351]

5) Hardener

A hardener can be used in each of image forming layer, protective layer, back layer, and the like.

As examples of the hardener, descriptions of various methods can be found in pages 77 to 87 of T.H. James, "THE THEORY OF THE PHOTOGRAPHIC PROCESS, FOURTH EDITION" (Macmillan Publishing Co., Inc., 1977). Preferably used are, in addition to chromium alum, sodium salt of 2,4-dichloro-6-hydroxy-s-triazine, N,N-ethylene bis(vinylsulfonacetamide), and N,N-propylene bis(vinylsulfonacetamide), polyvalent metal ions described in page 78 of the above literature and the like, polyisocyanates described in USP No. 4281060, JP-A No. 6-208193 and the like, epoxy compounds of USP No. 4791042 and the like, and vinyl sulfone based compounds of JP-A No. 62-89048.

[0352]

The hardener is added as a solution, and the solution is added to the coating solution for forming the protective layer 180 minutes before coating to just before coating, preferably 60 minutes before to 10 seconds before coating.

However, so long as the effect of the invention is sufficiently exhibited, there is no particular restriction concerning the mixing method and the conditions of mixing.

[0353]

As specific mixing methods, there can be mentioned a method of mixing in the tank, in which the average stay time calculated from the flow rate of addition and the feed rate to the coater is controlled to yield a desired time, or a method using static mixer as described in Chapter 8 of N. Harnby, M.F. Edwards, A.W. Nienow (translated by Koji Takahashi) "Liquid Mixing Technology" (Nikkan Kogyo Shinbun, 1989), and the like.

[0354]

6) Surfactant

[0355]

The photothermographic material of the invention may contain a surfactant for the purpose of improvement on coatability and a charging property. Examples of surfactants may include a nonionic surfactant, an anionic surfactant, a cationic surfactant and a fluorocarbon surfactant, any of which may be properly used. Concrete examples and patent related documents in which examples are described are as follows: fluorocarbon polymer surfactants described in JP-A No. 62-170950, USP No. 5380644 and the like; fluorocarbon surfactants described in JP-A Nos. 60-244945, 63-188135 and the like; polysiloxane based surfactants described in USP No. 3885965 and the like; and polyalkylene oxides and anionic surfactants described in JP-A 6-301140 and the like.

[0356]

In the invention, preferably used are fluorocarbon surfactants. Specific examples of fluorocarbon surfactants can be found in those described in JP-A Nos. 10-197985, 2000-19680, and 2000-214554. Polymer fluorocarbon surfactants described in JP-A 9-281636 can be also used preferably. The usage of fluorocarbon surfactant described in JP-A No. 2000-206560 is particularly preferred.

[0357]

7) Coating Solvent

Examples of the solvent include those described in Shin Han Yozai Pocketbook (New Edition, Solvent Pocketbook), Ohm Sha (1994), however, the present invention is not limited thereto. The solvent for use in the present invention preferably has a boiling point of 40°C to 180°C. Specific examples of the solvent include hexane, cyclohexane, toluene, methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, ethyl acetate, 1,1,1-trichloroethane, tetrahydrofuran, triethylamine, thiophene, trifluoroethanol, perfluoropentane, xylene, n-butanol, phenol, methyl isobutyl ketone, cyclohexanone, butyl acetate, diethyl carbonate, chlorobenzene, dibutyl ether, anisole, ethylene glycol diethyl ether, N,N-dimethylformamide, morpholine, propanesultone, perfluorotributylamine and water.

[0358]

8) Antistatic agent

The photothermographic material of the invention preferably contains an

electrically conductive layer including metal oxides or electrically conductive polymers. The antistatic layer may serve as an undercoat layer, or a back surface protective layer, and the like, but can also be placed specially. Examples of the antistatic layer in the invention include described in paragraph No. 0135 of JP-A No. 11-65021, JP-A Nos. 56-143430, 56-143431, 58-62646, and 56-120519, in paragraph Nos. 0040 to 0051 of JP-A No. 11-84573, US-P No. 5575957, and in paragraph Nos. 0078 to 0084 of JP-A No. 11-223898.

[0359]

9) Support

Typical support includes a polyester film, undercoated polyester film, poly(ethylene terephthalate) film, poly(ethylene naphthalate) film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film, and related or resin-like material, as well as glass, paper, metal, and the like. Flexible base material, particularly such that are partially acetylized, or baryta coated and/or α-olefin polymer laminated supports are used; in particular, paper supports coated with α-olefin polymer having 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymer, and the like, are typically used. The support may be transparent or opaque, but preferred is transparent.

[0360]

As the transparent support, favorably used is polyester, particularly, polyethylene terephthalate, which is subjected to heat treatment in the temperature range of from 130°C to 185°C in order to relax the internal strain caused by biaxial stretching and remaining inside the film, and to remove strain ascribed to heat

shrinkage generated during thermal development.

[0361]

In the case of a photothermographic material for medical use, the transparent support may be colored with a blue dye (for instance, dye-1 described in the Example of JP-A No. 8-240877), or may be uncolored. Examples of the support are described in paragraph No. 0134 of JP-A No.11-65021.

[0362]

As to the support, it is preferred to apply undercoating technology, such as water-soluble polyester described in JP-A No. 11-84574, a styrene-butadiene copolymer described in JP-A No. 10-186565, a vinylidene chloride copolymer described in JP-A No. 2000-39684 and in paragraph Nos. 0063 to 0080 of Japanese Patent Application No. 11-106881, and the like.

[0363]

10) Other additives

Furthermore, antioxidant, stabilizing agent, plasticizer, UV absorbent, or a coating aid may be added to the photothermographic material. Each of the additives is added to either of the photosensitive layer or the non-photosensitive layer. Reference can be made to WO No. 98/36322, EP No. 803764A1, JP-A Nos. 10-186567 and 10-18568, and the like.

[0364]

11) Coating method

The photothermographic material of the invention may be coated by any method. More specifically, various types of coating operations inclusive of extrusion coating, slide coating, curtain coating, immersion coating, knife coating, flow coating, or an extrusion coating using the type of hopper described in USP No. 2681294 are used. Preferably used is extrusion coating or slide coating described in pages 399 to 536 of Stephen F. Kistler and Petert M. Shweizer, "LIQUID FILM COATING" (Chapman & Hall, 1997), and most preferably used is extrusion coating.

[0365]

12) Wrapping material

In order to suppress fluctuation from occurring on the photographic performance during a preservation of the photosensitive material of the invention before thermal development, or in order to improve curling or winding tendencies, it is preferred that a wrapping material having low oxygen transmittance and/or vapor transmittance is used. Preferably, oxygen transmittance is 50 $mL/atm/m^2 \cdot day$ or lower at 25°C, more preferably, 10 $mL/atm/m^2/day$ or lower, and most preferably, 1.0 $mL/atm/m^2/day$ or lower. Preferably, vapor transmittance is 10 $g/atm/m^2/day$ or lower, more preferably, 5 $g/atm/m^2/day$ or lower, and most preferably, 1 $g/atm/m^2/day$ or lower. As specific examples of a wrapping material having low oxygen transmittance and/or vapor transmittance, reference can be made to, for instance, the wrapping material described in JP-A Nos.8-254793 and 2000-206653.

[0366]

13) Other applicable techniques

Techniques which can be used for the photothermographic material of the invention also include those in EP No. 803764A1, EP No. 883022A1, WO No. 98/36322, JP-A Nos. 56-62648, 58-62644, JP-A Nos. 09-43766, 09-281637, 09-297367, 09-304869, 09-311405, 09-329865, 10-10669, 10-62899, 10-69023, 10-186568, 10-90823, 10-171063, 10-186565, 10-186567, 10-186569 to 10-186572, 10-197974, 10-197982, 10-197983, 10-197985 to 10-197987, 10-207001, 10-207004, 10-221807, 10-282601, 10-288823, 10-288824, 10-307365, 10-312038, 10-339934, 11-7100, 11-15105, 11-24200, 11-24201, 11-30832, 11-84574, 11-65021, 11-109547, 11-125880, 11-129629, 11-133536 to 11-133539, 11-133542, 11-133543, 11-223898, 11-352627, 11-305377, 11-305378, 11-305384, 11-305380, 11-316435, 11-327076, 11-338096, 11-338098, 11-338099, 11-343420, Japanese Patent Application Nos. 2000-187298, 2000-10229, 2000-47345, 2000-206642, 2000-98530, 2000-98531, 2000-112059, 2000-112060, 2000-112104, 2000-112064 and 2000-171936.

[0367]

14) Color image formation

As a method of obtaining a color image using the photothermographic material of the invention, there is a method described in JP-A No. 7-13295, p. 10, left column line 48 to line 11, left column line 40. As stabilizers for color dye images, those exemplified in GBP No. 1326889, USP Nos. 3432300, 3698909, 3574627, 3573050, 3764337 and 4042394 can also be used.

In the case of a multi-color photothermographic material, in general, image forming layers are mutually discriminated and maintained by using a functional or

non-functional barrier layer between the image forming layers as described in USP No. 4460681.

[0368]

10. Image forming method

1) Exposure

Although the photosensitive material of the invention may be subjected to exposure by any methods, laser beam is preferred as an exposure light source. Particularly, silver halide emulsion of high content of silver iodide had a problem having low photosensitivity, but this problem was solved with the use of high illuminance like laser beam. And it made clear that it needs small amount of energy to record an image. Using thus strong light in a short time made it possible to achieve photosensitivity to the purpose.

[0369]

Especially, for giving the exposure intensity to provide maximum density (Dmax), the light intensity on the surface of the photographic material is preferably in the range of 0.1 W/mm^2 to 100 W/mm^2, more preferably 0.5 W/mm^2 to 50 W/mm^2, most preferably 1 W/mm^2 to 50 W/mm^2.

[0370]

As a laser beam according to the invention, preferably used is a gas laser (Ar^+, He-Ne, or He-Cd), a YAG laser, a pigment laser, or a laser diode. A laser diode and a second harmonics generator element can also be used. Preferred laser is determined corresponding to the peak absorption wavelength of spectral

sensitizer and the like, but preferred is a He-Ne laser of red through infrared emission, or a red laser diode; or a Ar^+, a He-Ne, or a He-Cd laser of blue through green emission, or a blue laser diode. Meanwhile, modules having a SHG (Second Hermonic Generator) chip and a laser diode which are integrated, or blue laser diode have been espcially developed recently, and thus laser output devices for short wavelength region have attracted the attention. Blue laser diode has been expected as a light source with increasing demand hereafter because image recording with high definition is possible, and increased recording density, as well as stable output with longer operating life are enabled. The peak wavelength of laser beam is 300 nm to 500 nm, preferably 400 nm to 500 nm, for blue; and 600 nm to 900 nm, preferably 620 nm to 850 nm, for red to near infrared.

[0371]

Laser beam which oscillates in a longitudinal multiple modulation by a method such as high frequency superposition is also preferably employed.

[0372]

2) Thermal development

Although the development of the photothermographic material of the invention is usually performed by elevating the temperature of the photothermographic material exposed imagewise, any method may be used for this thermal development process. The temperature for the development is preferably 80°C to 250°C, and more preferably 100°C to 140°C. Time period for the development is preferably 1 second to 180 seconds, and more preferably 10 seconds to 90 seconds.

[0373]

In the process for the thermal development, plate type heater process is preferred. Preferable process for the thermal development by a plate type heater may be a process described in JP-A NO. 11-133572, which discloses a thermal developing device in which a visible image is obtained by bringing a photothermographic material with a formed latent image into contact with a heating means at a thermal development region, wherein the heating means comprises a plate heater, and plurality of retainer rollers are oppositely provided along one surface of the plate heater, the thermal developing device is characterized in that thermal development is performed by passing the photothermographic material between the retainer rollers and the plate heater. It is preferred that the plate heater is divided into 2 to 6 portions, with the leading end having the lower temperature by 1°C to 10°C.

[0374]

Such a process is also described in JP-A NO. 54-30032, which allows for excluding moisture and organic solvents included in the photothermographic material out of the system, and also allows for suppressing the change of shapes of the support of the photothermographic material upon rapid heating of the photothermographic material.

[0375]

Further, in other heating methods, as described in specifications of U.S.P Nos. 440681 and 4374921, backside resistive heating layers are provided to

generate heat by charging an electric to heat the photoehermographic material.

[0376]

3) System

Examples of a medical laser imager equipped with a light exposing part and a thermal developing part include Fuji Medical Dry Laser Imager FM-DP L. In connection with FM-DP L, description is found in Fuji Medical Review No. 8, pages 39 to 55. It goes without mentioning that those techniques may be applied as the laser imager for the photothermographic material of the invention. In addition, the present photothermographic material can be also applied as a photothermographic material for the laser imager used in "AD network" which was proposed by Fuji Film Medical Co., Ltd. as a network system accommodated to DICOM standard.

[0377]

11. Application of the invention

The image forming method in which the photothermographic material of the invention is used is preferably employed as image forming methods for photothermographic materials for use in medical imaging, photothermographic materials for use in industrial photographs, photothermographic materials for use in graphic arts, as well as for COM, through forming black and white images by silver imaging.

[0378]

[EXAMPLES]

The present invention is specifically explained by way of Examples below, which should not be construed as limiting the invention thereto.

Example 1

1. Preparation of PET Support

Both surfaces of the PET film which was colored blue at the density 0.17 and had a thickness of 175 μm were treated to corona discharge treatment of 8 $W/m^2 \cdot min$.

[0379]

2. Coating of Back layer

In 830 g of MEK, 84.2 g of cellulose acetate butyrate (CAB381-20, produced by Eastman Chemical Co.) and 4.5 g of polyester resin (Vitel PE2200B, produced by Bostic Co.) were added and dissolved while stirring was carried out. To the solution, 43.2 g of methanol having dissolved therein 4.5 g of a fluorocarbon surfactant (Surflon KH40, product by Asahi Glass Co., Ltd.) and 2.3 g of another fluorocarbon surfactant (Megafac F120K, product by Dainippon Ink & Chemicals Inc.) was added. The resulting solution was thoroughly stirred until these were dissolved. Finally, 75 g of silica (Siloid 64X6000, product by W.R. Grace Co.) dispersed in methyl ethyl ketone to a concentration of 1% by mass using a dissolver-type homogenizer was added and the mixture was stirred to prepare a coating solution for a back layer.

The thus-prepared coating solution for the back layer was coated and dried by an extrusion coater, so as to provide a dry thickness of 3.5μm. Drying was performed for 5 minutes using air having a temperature of 100°C and a dew point

of 10°C.

[0380]

3. Image forming layer and surface protective layer

1) Preparation of silver halide emulsion

《Preparation of Silver Halide Emulsion-1》

To 1420 mL of distilled water was added 4.3 mL of a 1% by mass potassium iodide solution. Further, a liquid added with 3.5 mL of 0.5 mol/L sulfuric acid and 36.7 g of phthalated gelatin was kept at 42°C while stirring in a stainless steel reaction pot, and thereto were added total amount of: solution A prepared through diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 195.6 mL; and solution B prepared through diluting 21.8 g of potassium iodide with distilled water to give the volume of 218 mL, over 9 minutes at a constant flow rate. Thereafter, 10 mL of a 3.5% by mass aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by mass aqueous solution of benzimidazole was further added.

[0381]

Moreover, a solution C prepared through diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 317.5 mL and a solution D prepared through diluting 60 g of potassium iodide with distilled water to give the volume of 600 mL were added. A controlled double jet method was executed through adding total amount of the solution C at a constant flow rate over 120 minutes, accompanied by adding the solution D while maintaining the pAg at 8.1. Hexachloroiridium (III) potassium salt was added to give 1 x 10^{-4} mol per one mol

of silver at 10 minutes post initiation of the addition of the solution C and the solution D in its entirety. Moreover, at 5 seconds after completing the addition of the solution C, a potassium iron (II) hexacyanide aqueous solution was added at a total amount of 3×10^{-4} mol per one mol of silver. The mixture was adjusted to the pH of 3.8 with 0.5 mol/L sulfuric acid. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with 1 mol/L sodium hydroxide to produce a silver halide dispersion having the pAg of 8.0.

[0382]

The above-mentioned silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by mass methanol solution of 1,2-benzoisothiazoline-3-one, followed by elevating the temperature to 47°C. At 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added at 7.6×10^{-5} mol per one mol of silver. At additional 5 minutes later, a tellurium sensitizer C in a methanol solution was added at 2.9×10^{-4} mol per one mol of silver and subjected to aging for 91 minutes. Thereto was added 1.3 mL of a 0.8% by mass N,N'-dihydroxy-N",N"-diethylmelamine in methanol, and at additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution at 4.8×10^{-3} mol per one mol of silver, 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution at 5.4×10^{-3} mol per one mol of silver were added to produce a silver halide emulsion-1.

[0383]

Grains in thus prepared silver halide emulsion were pure silver iodide

grains having a mean sphere equivalent diameter of 0.040 μm, a variation coefficient of 18%. Grain size and the like were determined from the average of 1000 grains using an electron microscope.

[0384]

Further, as "a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which releases one or more electrons", the compounds Nos. 2, 20 and 26 were added respectively in the amount of 2×10^{-3} mol per one mol of silver halide.

[0385]

Thereafter, as "a compound having an adsorptive group and a reducible group", the compounds Nos. (19), (49), and (71) were added respectively in the amount of 8×10^{-3} mol per one mol of silver halide, as shown in Tables 2 and 3.

[0386]

《Preparation of Silver Halide Emulsion-2》

To 1421 mL of distilled water was added 3.1 mL of a 1% by mass potassium bromide solution. Further, a liquid added with 3.5 mL of 0.5 mol/L sulfuric acid and 31.7 g of phthalated gelatin was kept at 34°C while stirring in a stainless steel reaction pot, and thereto were added total amount of: solution A prepared through diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 95.4 mL; and solution B prepared through diluting 15.3 g of potassium bromide and 0.8 g of potassium iodide with distilled water to give the volume of 97.4 mL, over 45 seconds at a constant flow rate. Thereafter, 10 mL of

a 3.5% by mass aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by mass aqueous solution of benzimidazole was further added.

[0387]

Moreover, a solution C prepared through diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 317.5 mL and a solution D prepared through diluting 60 g of potassium iodide with distilled water to give the volume of 600 mL were added. A controlled double jet method was executed through adding total amount of the solution C at a constant flow rate over 120 minutes, accompanied by adding the solution D while maintaining the pAg at 6.3. Hexachloroiridium (III) potassium salt was added to give 1×10^{-4} mol per one mol of silver at 10 minutes post initiation of the addition of the solution C and the solution D in its entirety. Moreover, at 5 seconds after completing the addition of the solution C, a potassium iron (II) hexacyanide aqueous solution was added at a total amount of 3×10^{-4} mol per one mol of silver. The mixture was adjusted to the pH of 3.8 with 0.5 mol/L sulfuric acid. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with 1 mol/L sodium hydroxide to produce a silver halide dispersion having the pAg of 8.0.

[0388]

Other conditions were established similar to the preparation of silver halide emulsion-1 to produce a silver halide emulsion-2. Grains in thus prepared silver halide emulsion were grains, where 70 mol% of silver iodide layer was joining to 30 mol% of silver bromide layer, having a mean sphere equivalent

diameter of 0.040 μm, a variation coefficient of 10%. The portion wich has a silver iodide structure had a light absorption due to strong direct transition.

[0389]

Further, as "a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which releases one or more electrons", the compounds Nos. 2, 20 and 26 were added respectively in the amount of 2 x 10^{-3} mol per one mol of silver halide.

[0390]

Thereafter, as "a compound having an adsorptive group and a reducible group", the compounds Nos. (19), (49), and (71) were added respectively in the amount of 8 x 10^{-3} mol per one mol of silver halide, as shown in Tables 2 and 3.

[0391]

《Preparations of Silver Halide Emulsion-3》

Preparation of silver halide emulsion-3 was conducted in a similar manner to the preparation of silver halide emulsion-2 except that; changing the addition amount of potassium iodide and potassium bromide in the step of preparation of silver halide dispersion, and controlling the temperature in the step of grain growth in order to control the grain size.

[0392]

Grains in thus prepared silver halide emulsion were silver iodobromide grains containing 3.5 mol% of silver iodide. The grains had a mean sphere

equivalent diameter of 0.040 μm.

[0393]

Further, as "a compound that can be one-electron-oxidized to provide a one-electron oxidation product, which releases one or more electrons", the compounds Nos. 2, 20 and 26 were added respectively in the amount of 2 × 10^{-3} mol per one mol of silver halide.

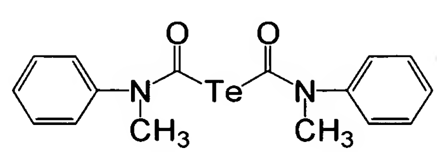
[0394]

Thereafter, as "a compound having an adsorptive group and a reducible group", the compound Nos. (19), (49), and (71) were added respectively in the amount of 8 × 10^{-3} mol per one mol of silver halide, as shown in Tables 2 and 3.

[0395]

[F34]

Tellurium Sensitizer C



[0396]

2) Preparations of Powdery Organic Silver Salt

《Preparations of Powdery Organic Silver Salt A1 to D1》

To 4720 mL of purified water were added behenic acid, arachidic acid and

stearic acid at 0.7552 mol in total with a ratio presented in Table 1. After dissolving at 80°C, 540.2 mL of a 1.5 N aqueous sodium hydroxide solution was added to the solution, and thereto was added 6.9 mL of concentrated nitric acid, followed by cooling to 55°C to obtain a solution of sodium salt of organic acid. While keeping the temperature of the sodium salt of organic acid solution at 55°C, 45.3 g of the aforementioned silver halide emulsion-1 and 450 mL of purified water were added thereto. The mixture was stirred with a homogenizer manufactured by IKA JAPAN Co. (ULTRA-TURRAXT-25) at 13200 rpm (corresponding to 21.1 kHz of mechanical vibration frequency) for 5 minutes. Then, 702.6 mL of a 1 mol/L silver nitrate solution was added thereto over 2 minutes, followed by stirring for 10 minutes to obtain an organic silver salt dispersion A1 to D1. Thereafter, the resulting organic silver salt dispersion was transferred to a washing vessel, and thereto was added deionized water followed by stirring. The mixture was allowed to stand still so that the organic silver salt dispersion was floatated, and thus water soluble salts present in the bottom part were removed. Then, washing with deionized water and drainage of the waste water was repeated until the electric conductivity of the waste water became 2 μS/cm. After performing centrifugal dewatering, drying in a circulating dryer was performed with warm air having the oxygen partial pressure of 10% by volume at 40°C until weight loss did not take place to obtain the powdery organic silver salts A1 to D1.

[0397]

[Table 1]

Table 1

Organic silver salt	Behenic acid (mol%)	Arachidinic acid (mol%)	Stearic acid (mol%)
A	25	55	20
B	54	29	17
C	60	28	12
D	90	10	0

[0398]

《Preparations of Powdery Organic Silver Salt A2 to D2》

Preparations of powdery organic silver salt A2 to D2 were conducted in the similar manner to the preparations of powdery organic silver salt A1 to D1, except that using silver halide emulsion-2 instead of using silver halide emulsion-1.

[0399]

《Preparations of Powdery Organic Silver Salt A3 to D3》

Preparations of powdery organic silver salt A3 to D3 were conducted in the similar manner to the preparations of powdery organic silver salt A1 to D1, except that using silver halide emulsion-3 instead of using silver halide emulsion-1.

[0400]

3) Preparation of Solution of Organic Silver Salt Dispersion Containing Photosensitive Emulsion

Polyvinyl butyral powder (Monsanto Co., Butvar B-79: Tg= 67°C) in an amount of 14.57 g was dissolved in 1457 g of methyl ethyl ketone (MEK), and thereto was gradually added 500 g of either one of the aforementioned powdery organic silver salts while stirring with a dissolver DISPERMAT CA-40M type

manufactured by VMA-GETZMANN Co., and thoroughly mixed to yield a slurry. The slurry was subjected to two passes dispersion with a GM-2 pressure type homogenizer manufactured by SMT Limited to prepare a photosensitive emulsion fluid dispersion. Upon this operation, the pressure for treatment with first-pass was set to be 280 kg/cm^2, whilst the pressure for treatment with second-pass was set to be 560 kg/cm^2.

[0401]

4) Preparations of Coating Solutions for Image Forming Layer

《Preparations of Coating Solutions for Image Forming Layer-1, -3, -5, -7, -9, -11, -13, -15, -17, -19, -21, -23, -25 to -36》

MEK was added in an amount of 15.1 g to aforementioned solution of photosensitive emulsion dispersion (50g), and the mixture was kept at 21°C while stirring with a dissolver type homogenizer at 1000 rpm. Thereto was added 390 μL of a 10% by mass methanol solution of an aggregate of: two molecules of N,N-dimethyl acetamide/ one molecule of oxalic acid/ one molecule of bromine, followed by stirring for 1 hour. Furthermore, thereto was added 494 μL of a 10% by mass methanol solution of calcium bromide, and the mixture was stirred for 20 minutes. Subsequently, 167 mg of a methanol solution containing 15.9% by mass of dibenzo-18-crown-6 and 4.9% by mass of potassium acetate was added to the mixture, followed by stirring for 10 minutes. Then, thereto was added 2.6 g of a MEK solution of 18.3% by mass 2-chlorobenzoic acid, 34.2% by mass salicylic acid-p-toluenesulfonate and 4.5% by mass 5-methyl-2-mercaptobenzimidazole, followed by stirring for one hour.

[0402]

Thereafter, the mixture was cooled to 13°C, and stirred for additional 30 minutes. After adding 13.31 g of polyvinyl butyral (Monsanto Co., Butvar B-79) while keeping the temperature at 13°C, followed by stirring for 30 minutes, 1.08 g of a 9.4% by mass tetrachlorophthalic acid solution was added thereto, followed by stirring for 15 minutes. While keeping stirring, 10.0 g of a 20% by mass MEK solution of the reducing agent 1,1-bis(2-hydroxy-3,5-dimetylphenyl)-2-methylpropane and a 1.1% by mass MEK solution of 4-methyl phthalic acid were added, then was subsequently added 1.5 g of 10% by mass Desmodur N3300 (Mobay, aliphatic isocyanate). Further, thereto was added 4.27 g of an MEK solution of 7.4% by mass tribromomethyl-2-azaphenylsulfone and 7.2% by mass phthalazine to obtain coating solutions for image forming layer-1, -3, -5, -7, -9, -11, -13, -15, -17, -19, -21, -23, -25 to -36.

[0403]

《Preparations of Coating Solutions for Image Forming Layer-2, -4, -6, -8, -10, -12, -14, -16, -18, -20, -22, and -24》

Preparations of coating solutions for image forming layer-, -2, -4, -6, -8, -10, -12, -14, -16, -18, -20, -22, and -24 were conducted in the similar manner to the preparations of abovementioed coating solution for image forming layer, except that using SBR (-St(75) -Bu(24) -AA(1)-: Tg= 29°C) instead of using powdery polyvinyl butyral (Tg= 67°C) as a binder.

[0404]

5) Preparation of Coating Solution for Surface Protective Layer

To 865 g of MEK was added, while stirring was continued, 96 g of cellulose acetate butyrate (manufactured by Eastman Chemical, CAB 171-15), 4.5 g of polymethyl methacrylate (manufactured by Rohm & Haas, PARALOID A-21), 1.5 g of 1,3-di(vinylsulfonyl)-2-propanol, 1.0 g of benzotriazole and 1.0 g of a fluorocarbon surfactant (manufactured by Asahi Glass Co., Ltd., SURFLON KH40), and dissolved, then, 30 g of a dispersion prepared by dispersing 13.6% by mass of cellulose acetate butyrate (manufactured by Eastman Chemical, CAB 171-15) and 9% by mass of calcium carbonate (manufactured by Speciality Minerals, Super-Pflex 200) in MEK by a dissolver type homogenizer at 8000 rpm for 30 minutes was added and stirring was carried out, to prepare a coating solution for surface protective layer.

[0405]

6) Coating

Coating solutions for image forming layer-1 to -36 and a coating solution for a surface protective layer described above were simultaneously applied to form multiple layers on the opposite surface to a back layer of a support by an extrusion coater, to produce photothermographic material-1 to -36. The image forming layer was coated so as to be an amount of silver coated as 1.9 g/m^2 and the surface protective layer to be a dry film thickness as 2.5 μm. Then, it was dried using an air of the temperature of 75°C and a due point of 10°C over 10 minutes.

[0406]

4. Exposure and Development

A NLMV 3000E laser diode fabricated by Nichia Corporation was mounted

as a laser diode beam source. Exposures of photothermographic material-1 to-36 were performed while setting or altering a photothermographic material surface intensity at 0 mW/mm^2 and from 1 mW/mm^2 to 1000 mW/mm^2. A light-emission wavelength of laser beam was 405 nm.

[0407]

Then, development was conducted at 124°C for 15 seconds using an automatic developing machine having a heat drum so that the surface protective layer of the photothermographic material and the drum surface came into contact. In this operation, the room for exposure and development had a temperature of 23°C and a relative humidity of 50% RH.

[0408]

5. Evaluation of Photographic Properties

The dentisy of the image obtained was measured with a densitometer, and a photographic characteristic curve representing a relationship between the common logarithm (log E) of a light exposure and the density was prepared.

Evaluations were conducted as described below.

1) Evaluation of fog

The optical density of the unexposed part was evaluated.

2) Evaluation of sensitivity

A sensitivity is defined as a reciprocal of an exposure value at which an optical density of Dmin(fog) + 1.0 is obtained. A sensitivity of the photothermographic material-1 is set to 100 and relative sensitivity value was shown. A larger relative sensitivity value means a higher sensitivity.

[0409]

3) Evaluation of dark stability

The developed images of the sample-1 to -36 were kept in condition of 60℃ and relative humidity of 50% for 72 hours. As for the photothermographic material which is inferior in dark stability, the fog degree of the unexposed part was increased. The fog increment amount at Dmin part after the above keeping with respect to the fog before keeping (ΔDmin) was defined as dark stability.

[0410]

The results obtained are shown in Tables 2 and 3.

[0411]

[Table 2]

Table 2

Photothermographic material No.	Silver halide emulsion		Compound having adsorptive group and reducible group	Silver salt of fatty acid		Binder (Tg)	Sensitivity	Fog	Dark stability (Δ Dmin)	Remarks
		Silver iodide content (mol%)			Silver behenate content (mol%)					
1	1	100	-	A	25	PVB(67°C)	100	0.24	0.10	Com. Example
2	1	100	-	A	25	SBR(29°C)	105	0.30	0.14	Com. Example
3	1	100	-	B	54	PVB(67°C)	95	0.18	0.03	Com. Example
4	1	100	-	B	54	SBR(29°C)	100	0.28	0.10	Com. Example
5	1	100	-	C	60	PVB(67°C)	90	0.18	0.02	Com. Example
6	1	100	-	C	60	SBR(29°C)	95	0.26	0.09	Com. Example
7	1	100	-	D	90	PVB(67°C)	65	0.18	0.02	Com. Example
8	1	100	-	D	90	SBR(29°C)	70	0.24	0.09	Com. Example
9	1	100	(19)(71)	A	25	PVB(67°C)	230	0.30	0.10	Com. Example
10	1	100	(19)(71)	A	25	SBR(29°C)	235	0.35	0.14	Com. Example
11	1	100	(19)(71)	B	54	PVB(67°C)	190	0.19	0.03	Present Invention
12	1	100	(19)(71)	B	54	SBR(29°C)	195	0.33	0.10	Com. Example
13	1	100	(19)(71)	C	60	PVB(67°C)	170	0.19	0.02	Present Invention
14	1	100	(19)(71)	C	60	SBR(29°C)	175	0.31	0.09	Com. Example
15	1	100	(19)(71)	D	90	PVB(67°C)	110	0.19	0.02	Com. Example
16	1	100	(19)(71)	D	90	SBR(29°C)	115	0.29	0.09	Com. Example
17	1	100	(19)(49)(71)	A	25	PVB(67°C)	260	0.30	0.10	Com. Example
18	1	100	(19)(49)(71)	A	25	SBR(29°C)	265	0.35	0.14	Com. Example
19	1	100	(19)(49)(71)	B	54	PVB(67°C)	220	0.19	0.03	Present Invention
20	1	100	(19)(49)(71)	B	54	SBR(29°C)	225	0.33	0.10	Com. Example

[0412] [Table 3]

Photothermographic material No.	Silver halide emulsion		Compound having adsorptive group and reducible group	Silver salt of fatty acid		Binder (Tg)	Sensitivity	Fog	Dark stability (ΔDmin)	Remarks
		Silver iodide content (mol%)			Silver behenate content (mol%)					
21	1	100	(19)(49)(71)	C	60	PVB(67°C)	200	0.19	0.02	Present Invention
22	1	100	(19)(49)(71)	C	60	SBR(29°C)	205	0.31	0.09	Com. Example
23	1	100	(19)(49)(71)	D	90	PVB(67°C)	135	0.19	0.02	Com. Example
24	1	100	(19)(49)(71)	D	90	SBR(29°C)	140	0.29	0.09	Com. Example
25	2	70	-	A	25	PVB(67°C)	80	0.23	0.12	Com. Example
26	2	70	-	C	60	PVB(67°C)	75	0.18	0.04	Com. Example
27	2	70	-	D	90	PVB(67°C)	50	0.18	0.04	Com. Example
28	2	70	(19)(49)(71)	A	25	PVB(67°C)	220	0.30	0.12	Com. Example
29	2	70	(19)(49)(71)	C	60	PVB(67°C)	180	0.19	0.04	Present Invention
30	2	70	(19)(49)(71)	D	90	PVB(67°C)	115	0.19	0.04	Com. Example
31	3	3.5	-	A	25	PVB(67°C)	50	0.23	0.17	Com. Example
32	3	3.5	-	C	60	PVB(67°C)	45	0.18	0.06	Com. Example
33	3	3.5	-	D	90	PVB(67°C)	35	0.18	0.06	Com. Example
34	3	3.5	(19)(49)(71)	A	25	PVB(67°C)	130	0.30	0.17	Com. Example
35	3	3.5	(19)(49)(71)	C	60	PVB(67°C)	100	0.19	0.06	Present Invention
36	3	3.5	(19)(49)(71)	D	90	PVB(67°C)	65	0.19	0.06	Com. Example

[0413]

From results of Tables 2 and 3, the photothermographic material of the invention has a high sensitivity with a low fogging while exhibiting excellent in dark stability. In the case where the content of silver behenate is 30 mol% or less and the sample comprises a compound having an adsorptive group and a reducible group, the increment amount of fogging is large, but in the case where the content of silver behenate is 30 mol% or more the increase of fog is almost not observed and high sensitivity has obtained. This effect of the content of silver behenate upon the photothermographic material comprising a compound having an adsorptive group and a reducible group was an unexpected result.

[0414]

It was an unexpected result that quite a low increment of fogging and a high sensitivity are obtained by use of a compound having an adsorptive group and a reducible group in the case the glass transition temperature (Tg) of the binder is 45℃ or more.

[0415]

Thus, the best effect of the invention was obtained by concomitant use of a silver behenate in a content of 30 mol% to 80 mol%, a binder having Tg of 45℃ or more and a compound having an adsorptive group and a reducible group.

[0416]

Further, in the case where the silver halide having high silver iodide content is used, a photothermographic material excellent in dark stability was

obtained.

[0417]

In accordance with the present invention, a photothermographic material in which dark stability after the completion of heat-developmemt treatment is improved.

[DOCUMENT NAME] ABSTRACT OF THE DISCLOSURE

[SUMMARY]

[OBJECT] To provide a photothermographic material which has high sensitivity and low fogging and in which dark stability after the completion of heat-developmemt treatment is improved.

[MEANS FOR SOLUTION]

A photothermographic material comprising, on a support, a photosensitive silver halide, a non-photosensitive organic silver salt, a reducing agent and a binder, wherein the photothermographic material comprises a compound having a group adsorptive to silver halide and a reducible group or a precursor of the compound, a silver behenate content of the non-photosensitive organic silver salt is at least 30% by mole and less than 80% by mole, and the binder has a glass transition temperature (Tg) of 45°C or higher.

[SELECTED FIGURE] NONE